GAS ANALYSIS

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GAS ANALYSIS

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PREFACE

Since the publication of the earlier edition of this book in 1913, many important investigations in the field of Gas Analysis have appeared, and new lines of experimental investigation have been developed. Among the new topics that have been included in the present volume are methods of gas analysis that are based on thermal conductivity, new procedures for the determination of the specific gravity of gases, a description of the interferometer and its employment, and a detailed discussion of specific absorption and of the correction of barometric readings. Several methods that were given in the earlier edition, but which are no longer used or have been superceded by more satisfactory procedures, are now omitted.

In gas analysis the accuracy of the determination is probably dependent to a greater degree upon the manipulatory skill with which the work is performed than in any other branch of chemical analysis. It is for this reason that the manipulation of each of the more generally used types of apparatus is described at length.

The findings of able investigators corcerning certain methods or reactions are at times directly contradictory. Decision as to which of such statements is correct, and which procedure should be recommended, could properly be based only upon careful experimental tests which would have called for prolonged study of the points in controversy. In such cases, therefore, we have given the views of the various writers, with full references to the original articles, leaving to the reader the selection of the method that he will employ.

L. M. Dennis
M. L. Nichols

July, 1929

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CONTENTS

CHAPTER I

THE COLLECTION AND STORAGE OF GASES

PAGE
Drawing off the Sample 1
Sample Tubes 3
Aspirators 6
Mercury Pump 8
Collection of Gases from Springs 11
Collection of Gases Dissolved in Liquids 12
Collection of Gases from Reactions in Sealed Tubes . . . 15
Extraction of Gases from Minerals 16
Gasometers 18

CHAPTER II

THE MEASUREMENT OF LARGE SAMPLES OF GAS

Gas Meter 21
Dry Gas Meter 24
Flow Meter 26
Rotameter 27

CHAPTER III

THE REDUCTION OF A VOLUME OF GAS TO STANDARD CONDITIONS

Effect of Pressure 29
Effect of Temperature 29
Barometry 33
Aneroid Barometer 33
Mercurial Barometer 34
Correction of Barometric Readings 34
Correction for Gravity 34

PAGE
Correction for the Temperature of the Mercury 36
Correction for the Measured Height of the Mercury Column. 37
Expansion of the Scale 37
Vapor Pressure of Mercury 38
Capillary Depression 38
Complete Correction of Barometric Readings 43
Residual Gas Air 43
Manometry 44
McLeod Gauge 45

CHAPTER IV

THE DETERMINATION OF THE DENSITY AND THE SPECIFIC GRAVITY OF GASES

Determination of the Density of a Gas 49
Determination of the Specific Gravity of a Gas 49
  By Direct Weighing 49
  By Effusion Method 50
  By Buoyant Effect 53

CHAPTER V

ARRANGEMENTS AND FITTINGS OF THE LABORATORY

Laboratory for Gas Analysis 56

CHAPTER VI

APPARATUS FOR GAS ANALYSIS WITH WATER AS THE CONFINING LIQUID

Hempel Simple Gas Burette 58
Hempel Simple Absorption Pipettes 60
Hempel Simple Absorption Pipette for Liquid Reagents . . 60
Hempel Absorption Pipette with Absorption Bulb 62
Hempel Simple Absorption Pipette for Solid and Liquid Reagents 63
Hempel Double Absorption Pipettes 63

PAGE
Hempel Double Absorption Pipette for Liquid Reagents . . 64
Hempel Double Absorption Pipette for Solid and Liquid Reagents 65
Manipulation of the Hempel Apparatus 66
Filling Burette with Confining Liquid 67
Measurements of 100 cc. 67
Absorption of a Gas 68
Accuracy of Analyses with the Hempel Apparatus . . . 71
Other Forms of Apparatus 72
Orsat Apparatus 73
Manipulation of Orsat-Dennis Apparatus 79
Bureau of Mines Orsat Apparatus 82
Manipulation 84

CHAPTER VII

FACTORS AFFECTING THE ACCURACY OF ANALYSES OF GASES

Specific Absorption of the Reagent 85
Changes of Temperature and Pressure 86
Changes in the Water-Vapor Content 87
Solubility of Gases in the Confining Liquid 87
Solubility of the Gases in the Different Absorbents . . . 88
Graduation of Burettes 88
Calibration of Burettes 89
Capillary Error of the Apparatus Used 91
Running-down of the Confining Liquid 93

CHAPTER VIII

THE HEMPEL APPARATUS FOR EXACT GAS ANALYSIS WITH MERCURY AS THE CONFINING LIQUID

Gas Burettes with Correction for Variations in Temperature and Barometric Pressure 95
Absorption Pipettes 101
Simple Mercury Absorption Pipette 101

PAGE
Simple Mercury Absorption Pipette for Solid and Liquid Reagents 102
Mercury Absorption Pipette with Absorption Bulb . . . 102
Bone and Wheeler's Apparatus 103

CHAPTER IX

THE CONSTRUCTION AND CONNECTION OF APPARATUS

Glass Blowing 105
Mounting of Apparatus 106
Rubber Connections 106
Mercury Seals 107
Ground-Glass Joints 107
Glass to Metal Joints 108
Stopcocks 108
Lubrication of Stopcocks 108
Mercury Float Valve 110

CHAPTER X

PURIFICATION OF MERCURY

Purification of Mercury by Nitric Acid 113
Purification of Mercury by Concentrated Sulphuric Acid and Mercurous Sulphate 114
Purification of Mercury by Distillation 115

CHAPTER XI

ABSORPTION APPARATUS FOR USE WITH LARGE VOLUMES OF GAS

Friedrichs Spiral Gas Washing Bottle 119
Winkler Absorption Apparatus 121

CHAPTER XII

THE COMBUSTION OF GASES

Possibilities and Limitations of the Combustion Method . . 123
Gaseous Hydrocarbons and Nitrogen 132

PAGE
Identification of Gaseous Hydrocarbons 134
Molecular Volumes of Gases 134

CHAPTER XIII

THE DETERMINATION OF GASES BY COMBUSTION

Analysis by Explosion 138
Explosion Pipette for Technical Gas Analysis 138
Proportion of Gases in Analysis by Explosion 140
Formation of Oxides of Nitrogen 141
Induction Coil 141
Preparation of Pure Hydrogen and Oxy-Hydrogen Gas . . 142
Analysis by Combustion 143
Combustion with an Electrically Heated Platinum Spiral . . 143
Combustion Pipette 143
Manipulation of the Combustion Pipette 145
Formation of Oxides of Nitrogen in Combustion Pipette . . 148
Combustion with Platinum Capillary Tube 149
Fractional Combustion with Platinum or Palladium Asbestos. 151
Fractional Combustion of Hydrogen with Palladium Black . 155
Fractional Combustion of Hydrogen with Copper Oxide . . 157

CHAPTER XIV

PROPERTIES OF THE VARIOUS GASES AND METHODS FOR THEIR DETERMINATION

Oxygen 171
Properties of Oxygen 171
Detection and Determination of Small Quantities of Oxygen. 171
Determination of Oxygen 172
Determination of Oxygen by Combustion 172
Determination of Oxygen with Copper Eudiometer . . . 173
Determination of Oxygen by Absorption 174
Alkaline Pyrogallol 174
Phosphorus 181
Copper 184
Solutions of Ferrous Salts 186
Sodium Hyposulphite 187

PAGE
Chromous Chloride 188
Ozone 189
Properties of Ozone 189
Detection of Ozone 189
Determination of Ozone 191
Hydrogen 197
Properties of Hydrogen 197
Detection of Hydrogen 198
Determination of Hydrogen by Absorption 199
Determination of Hydrogen by Explosion 205
Determination of Hydrogen with Combustion Pipette . . . 206
Fractional Combustion of Hydrogen 208
Nitrogen 209
Properties of Nitrogen 209
Absorption of Nitrogen 209
Nitrous Oxide 215
Properties of Nitrous Oxide 215
Detection of Nitrous Oxide 216
Determination of Nitrous Oxide 216
Nitric Oxide 220
Properties of Nitric Oxide 220
Detection of Nitric Oxide 220
Determination of Nitric Oxide 222
Nitrogen Peroxide 228
Properties of Nitrogen Peroxide 228
Determination of Nitrogen Peroxide 228
Ammonia 229
Properties of Ammonia 229
Detection of Ammonia 229
Determination of Ammonia 230
Carbon Dioxide 231
Properties of Carbon Dioxide 231
Determination of Carbon Dioxide 231
Carbon Monoxide 232
Properties of Carbon Monoxide 232
Detection of Carbon Monoxide by Blood Spectrum 233
Detection of Carbon Monoxide by Means of Iodine Pentoxide. 238
Other Methods of Detection 239

PAGE
Determination of Carbon Monoxide by Absorption . . . 240
Determination of Carbon Monoxide by Means of Iodine Pentoxide 246
Colorimetric Determination of Carbon Monoxide . . . 249
Determination of Carbon Monoxide by Fractional Combustion. 253
Methane 254
Properties of Methane 254
Detection of Methane 255
Determination of Methane 255
Heavy Hydrocarbons 259
Absorption of Heavy Hydrocarbons 260
Ethylene 262
Properties of Ethylene 262
Determination of Ethylene by Absorption 262
Determination of Ethylene in Presence of Acetylene . . . 263
Separation of Ethylene from Benzene 263
Separation of Ethylene from Butylene 264
Propylene 264
Acetylene 264
Properties of Acetylene 264
Determination of Acetylene 265
Cyanogen 268
Properties of Cyanogen 268
Detection of Cyanogen 268
Determination of Cyanogen 270
Detection and Determination of Cyanogen in Presence of Hydrogen Cyanide 272
Hydrogen Cyanide 275
Properties of Hydrogen Cyanide 275
Detection of Hydrogen Cyanide 275
Detection of Hydrogen Cyanide in Air 276
Determination of Hydrogen Cyanide 277
Hydrogen Sulphide 278
Properties of Hydrogen Sulphide 278
Detection of Hydrogen Sulphide 278
Determination of Hydrogen Sulphide 279
Carbon Disulphide 281
Properties of Carbon Disulphide 281

PAGE
Detection of Carbon Disulphide 281
Determination of Carbon Disulphide 282
Sulphur Dioxide 283
Properties of Sulphur Dioxide 283
Determination of Sulphur Dioxide 284
Carbon Oxysulphide 290
Properties of Carbon Oxysulphide 290
Determination of Carbon Oxysulphide 292
Fluorine 294
Determination of Fluorine 294
Chlorine 297
Properties of Chlorine 297
Determination of Chlorine 297
Hydrogen Chloride 301
Properties of Hydrogen Chloride 301
Determination of Hydrogen Chloride 302
Phosgene 302
Properties of Phosgene 302
Detection of Phosgene 302
Determination of Phosgene 303
Methyl Chloride 303
Properties of Methyl Chloride 303
Determination of Methyl Chloride 304
Silicon Tetrafluoride 305
Properties of Silicon Tetrafluoride 305
Determination of Silicon Tetrafluoride 305
Phosphine 305
Properties of Phosphine 305
Determination of Phosphine 306
Arsine 308
Properties of Arsine 308
Detection of Arsine 308
Determination of Arsine 309
Stibine 309
Properties of Stibine 309
Determination of Stibine 309
Dichloro-ethylsulphide (Mustard Gas) 310

CHAPTER XV

FLUE GAS ANALYSIS

PAGE
Sampling of Flue Gas 312
Analysis of Flue Gas 313
Automatic Flue Gas Analysis 315
Determination of Carbon Dioxide from Specific Gravity . . 316
Determination of Carbon Dioxide by Absorption 318
Determination of Carbon Dioxide by Thermal Conductivity . 323
Determination of Carbon Dioxide by Optical Refractivity . . 324
Determination of Carbon Dioxide by Electrometric Methods . 325
Flue Gas Calculations 325
Weight of Air for Combustion 326
Excess Air 327
Weight of Flue Gas 329
Heat Loss in Flue Gas 330

CHAPTER XVI

ILLUMINATING GAS—FUEL GAS

Coal Gas—Natural Gas

Coal Gas 334
Determination of the Illuminating Power of Coal Gas . . . 335
Determination of the Specific Gravity of Coal Gas . . . 336
Gas-Volumetric Analysis of Coal Gas 336
Determination of the Absorbable Gases 337
Carbon Dioxide 337
Benzene 338
Absorption of Benzene by Alcohol 338
Absorption of Benzene with Nickel Solution 339
Condensation of Benzene 341
Absorption of Benzene by Paraffin Oil 342
Determination of Benzene as Dinitrobenzene 343
Separation of Benzene from Ethylene 343
Differential Pressure Method 344
Adsorption by Charcoal 344
Other Heavy Hydrocarbons 344

PAGE
Oxygen 345
Carbon Monoxide 345
Hydrogen, Methane (and Ethane), and Nitrogen 345
Nitrogen 347
Determination of Naphthalene in Coal Gas 348
Determination of Total Sulphur in Coal Gas 350
Determination of Sulphur by the U. S. Bureau of Standards (Drehschmidt) Method 351
Gravimetric Determination 355
Volumetric Determination 356
Turbidimetric Determination 358
Determination of Sulphur by Referees Method 359
Determination of Cyanogen in Coal Gas 362
Determination of Tar Vapors 362
Natural Gas 362

CHAPTER XVII

THE DETERMINATION OF THE HEATING VALUE OF GAS

Continuous Flow Calorimeters 365
Preparation of Apparatus 367
Determination of the Heating Value of the Gas 371
Accuracy of Calorimeters 372
Heat of Combustion 373
Calculation of Observed Heating Value 374
Calculation of Total Heating Value 376
Calculation of Net Heating Value 378
Determination of the Heating Value of Liquid Fuels . . . 379
Discontinuous Calorimeters 381
Automatic and Recording Gas Calorimeters 381
Calculation of Heating Value 384

CHAPTER XVIII

ACETYLENE

Impurities in Commercial Acetylene 385
Sampling of Calcium Carbide 385

PAGE
Determination of Hydrogen in Acetylene 386
Determination of Methane in Acetylene 386
Determination of Oxygen and Nitrogen in Acetylene . . . 387
Determination of Ammonia in Acetylene 387
Determination of Phosphine in Acetylene 387
Determination of Volume of Acetylene Evolved from Sample of Carbide 392
Determination of Sulphur in Acetylene 393
Determination of Silicon Hydride in Acetylene 393
Determination of Carbon Monoxide in Acetylene 394

CHAPTER XIX

EXAMINATION OF ATMOSPHERIC AIR

Composition of Atmospheric Air 395
Determination of Moisture in the Atmosphere 396
Absolute and Relative Humidity 396
Wet and Dry Bulb Thermometers 396
Psychrometers 397
Manipulation of the Psychrometer 398
Calculation of Results 399
Other Instruments 401
Determination of Carbon Dioxide in the Atmosphere . . . 402
Methods Employed in Determination of Carbon Dioxide in Air. 403
Hesse Method 403
Solutions used in the Hesse Method 404
Collection of Samples of Air 404
Manipulation 405
Calculation of Results 407
Pettersson-Palmqvist Method 408
Anderson's Modification of the Pettersson-Palmqvist Apparatus 412
Haldane Apparatus 417

CHAPTER XX

GAS–VOLUMETRIC ANALYSIS

Nitrometers 422
Lunge Nitrometer 422

PAGE
Manipulation of the Lunge Nitrometer 423
Lunge Gas Volumeter 425
Nitrometer 428
Du Pont Nitrometer 432
Standardization 434
Azotometer 436

CHAPTER XXI

PHYSICAL METHODS OF GAS ANALYSIS

Refractivity 437
Interferometer 439
Calibration of the Interferometer 442
Operation 443
Applications 444
Thermal-Conductivity 444
Calibration 451
Unbalanced Bridge 452
Balanced Bridge 452
Applications 453
Vapor Pressure, Fractional Distillation at Low Temperatures and Pressures 455
Diffusion 458
Other Methods 458

CHAPTER XXII

MICRO-ANALYSIS OF GASES

Method of Constant Volume 459
Method of Constant Pressure 463

APPENDIX

Atomic Weights, 1928 465
Theoretical Densities of Gases 466
Reduction of Gas Volume to 0° and 760 mm. 467

PAGE
Tension of Aqueous Vapor from — 2° C. + 34° C. 471
Tension of Aqueous Vapor from 32° F. — 94°F. 473

Index of Authors' Names 477
Index of Subjects 488

CHAPTER I

THE COLLECTION AND STORAGE OF GASES

The determination of the composition of a gas mixture involves two distinct operations, the collection of the sample and its analysis. Of the two operations the sampling is usually the more difficult and also the more important, because if it is not properly done, the analyses will be of no value and it may be impossible to secure a duplicate sample.

It is essential that the sample shall represent as closely as possible the composition of the gas at the place of sampling, and the apparatus which is used must be correctly adapted to this purpose.

Drawing off the Sample.—The collection of a sample of gas from a pipe, conduit, or furnace is usually accomplished by inserting into the chamber a tube of suitable material, and drawing off the gas either into a sampling tube or bottle, or directly into the apparatus in which the gas mixture is to be analyzed. In all cases the sampling tube must be of a material that will not affect the composition of the gas which is drawn through it. If the gas is at a comparatively low temperature, it may be drawn off through a tube of glass. At temperatures that do not exceed 300°, a small lead pipe will be found convenient because of its flexibility. Uncooled iron tubes should not be used at temperatures above 200° because the iron[1] will react with the carbon dioxide and change the composition of the sample. At high temperatures porcelain, alundum, or quartz tubes may be employed. If the gases are very hot, the tube should be surrounded by a second tube through which cold water is kept circulating. A satisfactory form of such a tube is shown in Fig. 1.[2] It consists of the tubes *A* and *C*, and a third tube *E* lying between *A* and *C*, to which the side arm *B* is attached. The outside tube *C* is usually made of iron and the tube *E* of copper. The inner tube *A* may be of copper, iron, or quartz.[3] The tube *A*, through which the gas sample is drawn, is about 5 mm. internal diameter. The tubes are kept cool by running water which enters through *B*, flows through *C*, and escapes through the outlet *D*. A tube of glass, iron, or lead carrying a short side tube is attached to *A*, and its further end is connected with an aspirator. The delivery tube should be so placed that there is a gradual drop towards the aspirator and it should have no bends or hollows where condensed water can accumulate.[4] If such a "pocket" is unavoidable, it should be equipped with a drain cock and water trap. The sample of gas to be analyzed is drawn off through this tube into a sample tube or a gas burette, as desired.

---

[1] Fischer, *Technologie der Brennstoffe* (1880), p. 221; Edwards, *Chem. Abst.*, **16**, 1851 (1922), however, states that it is quite safe to use iron sampling tubes at temperatures not exceeding 450° to 500°.

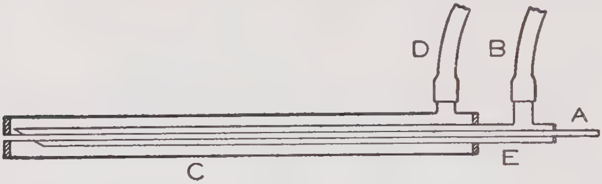

FIG. 1

Gas mixtures that are to be subjected to chemical analysis should never be passed through long pieces of rubber tubing. Rubber is not only porous, but it also may absorb certain constituents of the gas mixture. These absorbed gases or even the air that a fresh piece of rubber tubing contains will cling tenaciously to the walls of the tube, and they will slowly mix with a gas mixture of other composition that is passed through the tube. If for any reason the use of a long piece of rubber tubing cannot be avoided in the collection or transfer of a sample of gas, the rubber tube should be vigorously rolled between the palms of the hands while the sample is flowing through it, in order to detach the gas adhering to its walls. The gas that passes through the tube during this operation should of course be discarded.

---

[2] Winkler, *Lehrbuch der technischen Gasanalyse* (1885), p. 9; Kreisinger and Ovitz, *Bureau of Mines, Bulletin 97* (1915), p. 41.

[3] Frazer and Hoffman, *Bureau of Mines, Bulletin 12* (1911).

[4] Shurgar, *Elec. World*, **86**, 418 (1925), recommends putting an enlarged section of pipe through the furnace wall to prevent this trouble.

When short pieces of rubber tubing are used for connecting tubes of other material, the ends of the tubes should be brought together under the rubber connector.

A sample of the gaseous products of combustion from a heating apparatus should be drawn from the back of the fire chamber: further up in the flue, the gas will usually be found to contain a considerable quantity of air because of the porosity of the wall.

A gas mixture flowing through a large pipe frequently varies in composition from the middle of the pipe toward its sides. Many types of sampling tubes have been devised to secure, so far as possible, a sample that will represent the average composition of the mixture. These include the multiple tube,[5] the perforated tube,[6] and slit-tube samplers. It is quite impossible to give general directions that will apply in all cases. The type of sampling tube to be used, and the position of the sampling tube in the gas supply, must be adapted to the special conditions. It is essential, however, that the sampling tube should be fastened into the flue or pipe with an air-tight joint. It has been found[7] that in some instances a simple open-tube sampler placed in the center of the flue gave as correct a sample as any of the other devices.

Sample Tubes.—If the place where the gases are to be collected is directly accessible, as, for example, in the examination of mine gases, small sample tubes made in the laboratory from easily fusible glass tubing may be used. The form devised by Hempel for his researches "Upon the Composition of the Atmosphere at Different Parts of the Earth" is shown in Fig. 2. The constrictions *A*, *B*, and *C* are about one mm. in diameter. The tubes are heated in an air bath in the laboratory at 200°, and are then exhausted with a mercury air-pump and fused at *C*. By simply breaking the tube at *B*, it fills instantly and completely with the air in question. The tube is then closed with a rubber cap, and is sealed off at *A* over a candle. It has been found [8] satisfactory to seal the ends of these tubes with specially prepared wax. The exhausting with the air-pump has the advantage of rendering one less dependent upon the care of the person who fills the tubes. If, however, it is desired to avoid this exhausting, the tubes are given the form shown in Fig. 3. To fill such a tube, the gas to be examined is drawn through it and the tube is then sealed at *A* and *B* by fusion in a candle flame. Such tubes can safely be shipped by packing them in boxes that have a separate compartment for each tube.

---

[5] White, *Gas and Fuel Analysis* (1920), p. 4.

[6] Kreisinger and Ovitz, *Bureau of Mines, Bulletin 97* (1915), pp. 11, 52; Camp, *Met. Chem. Eng.*, **9**, 303 (1911).

[7] Swain, *J. Am. Soc. Mech. Eng.*, **38**, 978 (1916).

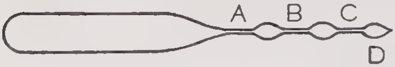

FIG. 2

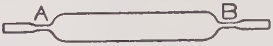

FIG. 3

A somewhat more convenient tube for collecting gas samples and transporting them to the laboratory for analysis is that shown in Fig. 4. The tubes used in the Cornell laboratory vary from 16 cm. x 3.5 cm. (capacity about 110 cc.) to 25 cm. x 4.5 cm., the stopcocks have a bore one mm. in diameter, and ends of the tube beyond the stopcocks are capillary tubes of six mm. external diameter and one mm. bore, and about four cm. long. If the stopcocks are well made and carefully lubricated, and are fastened securely in place after the tube is filled with the gas, a sample may be kept for a considerable length of time in such a tube without undergoing appreciable change, provided the gas mixture does not act upon the lubricant of the stopcocks.

---

[8] Burrell, Siebert, and Jones, *Bureau of Mines, Bulletin 197* (1926), p. 4.

In equipping a laboratory it is also well to provide some of these sampling tubes with tail-stoppers (Fig. 5). Such stopcocks render easy the elimination of the dead space in the end capillary tubes when the sample is transferred to the gas burette (see p. 67), but as they are more liable to leak than are the single bore stopcocks, tubes that are fitted with them, while more useful in the laboratory, are not so well suited to the transport of gas samples.

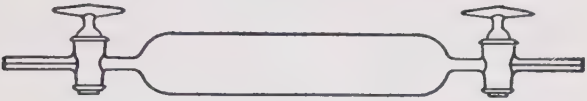

FIG. 4

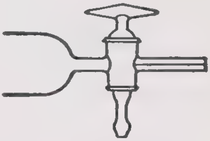

FIG. 5

These tubes are filled with the gas sample by drawing it through the tube until the air that was originally in the tubes is entirely displaced. Naturally this presupposes that large amounts of gas are at one's disposal. If only a small quantity of gas is available, the tube is first filled with water or mercury and this is then displaced by the gas. Water can be used only when it is first saturated with the gas mixture that is being sampled, and if any of the constituents of the gas mixture are fairly soluble in water, as, for example, ammonia or carbon dioxide, mercury must be employed even if only approximately accurate results are desired.

It is frequently the case that an average sample of the gases passing through a flue or pipe during a period of several hours is desired. Since carbon dioxide is always present in flue gases, mercury must be used as the confining liquid in the sample tube. The weight and costliness of mercury make it necessary that the sample tube be small, and this in turn renders it imperative that the dead space between the sample tube and main tube be eliminated and that it be impossible for the gas in the sampling tube to diffuse back into the main tube or to be drawn back into the main by a sudden drop in pressure. These conditions are fulfilled by the clever device of Huntly[9] which is shown in Fig. 6. The tube[10] is first filled with mercury up to the top of the bore of the upper stopcock, and both stopcocks are closed. The capillary *A* is then connected with the branch from the main tube, and the stopcock turned so that *A* communicates with *B*. The air in *A* is thus driven out through *B*. If the pressure in the main is less than that of the atmosphere, suction must be applied at *B*. The upper stopcock is then turned through 180° to connect *A* with *C*, and the lower stopcock is carefully opened to such an extent as will give the desired speed of flow. Huntly states that "it has been found by trial that the rate at which the gas is drawn in is constant throughout within one per cent."

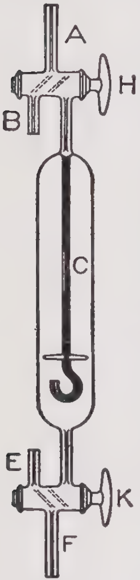

FIG. 6

If the tube is to be shipped to the laboratory after the sample has been taken, some mercury should be left in the capillary tube above the stopcock *K*, and the tube should be placed in a frame that will support it in an upright position.[11]

Aspirators.—If the gases to be collected have a pressure less than the prevailing atmospheric pressure, an aspirator must be employed to draw them over into the sampling apparatus. The simplest form of aspirator consists of two interchangeable bottles of equal size and of the same width of neck, as shown in Fig. 7. The water flows from the upper bottle *A* through the rubber siphon tube *E* into the lower bottle *C* and by so doing draws the gas sample through the tube F. When the bottle *A* is empty, *C* is full and they can be interchanged and the aspirating of the gas continued. This arrangement gives a constant change in the effective head of water due to the lowering and raising of the water levels in *A* and *C*. This could be corrected[12] by extending the tube *F* to the bottom of bottle *A* and cutting off the glass tube in *C* at the stopper, but if the sample is being collected in *A*, this procedure introduces a greater error because of the high solubility in water of some gases, such as carbon dioxide.

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[9] *J. Soc. Chem. Ind.*, **29**, 312 (1910).

[10] Huntly does not give the dimensions of the tube. If the wide part of the tube were about 18 cm. long and 3.5 cm. diameter, it would contain quite a little more than 100 cc., an amount sufficient for the analysis.

[11] In *Bulletin No. 12 of the Bureau of Mines* (1911), Frazer and Hoffman describe a sampling tube that is patterned after that of Huntly, but as it is not fitted with two-way stopcocks, it does not eliminate the dead space in the capillary tubes.

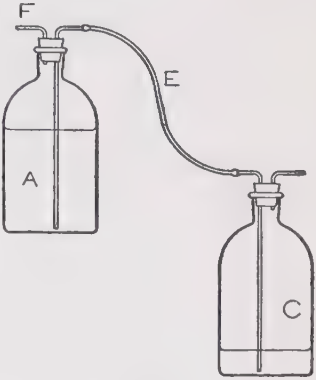

FIG. 7

In the ordinary two-bottle method of aspirating, the effective head of suction varies, and many forms of apparatus[13] have been devised with the object of securing an average sample of gas, taken at a uniform rate over any specified period of time.

Small rubber suction bulbs may at times be found useful for drawing a gas mixture into the sampling tube, which should be placed before the bulb to avoid contact of the gas with the rubber. If running water or steam is available, a water suction pump of glass or metal, or a steam ejector[14] may conveniently be employed as an aspirator.

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[12] Swain, *Am. Gas. Eng. J.*, **106**, 274 (1917), states that this method will never give an exactly correct sample due to the fact that the rates of flow in the gas main and sampling tube are not proportional.

[13] Kershaw, *Fuel, Water and Gas Analysis* (1907), p. 114; Gray, *J. Soc. Chem. Ind.*, **32**, 1092 (1913); Benzant, *Gas J.*, **156**, 433 (1921); Schumacher, *Gas u. Wasserfach*, **65**, 218 (1922); Goldsmith, *Gas J.*, **168**, 847 (1924); Dobson, *J. Chem. Soc.*, **125**, 1968 (1924); Plenz, *Gas u. Wasserfach*, **68**, 810 (1925); Gay, *Gas World*, **59**, 863.

[14] Kreisinger and Ovitz, *Bureau of Mines, Bulletin 97* (1915), p. 13.

When the sampling extends over a long period of time, and the sample is taken by direct passage into a sample tube, the flow of the gas through the sampling tube is so slow that variations of pressure in the main or flue render the sample unreliable. In this case it is advisable to use additional apparatus as shown in Fig. 8. *B* is a manometer to indicate any obstruction in the system, *C* is a bubbling-bottle, and *D* is a pressure regulator. The sample tube is attached to *A*, and a portion of the gas being drawn out by the aspirator is removed through *A* for analysis.

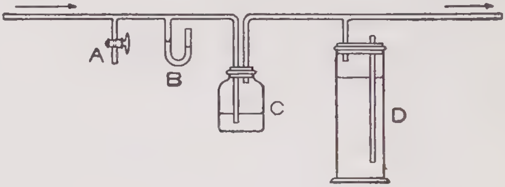

FIG. 8

The Mercury Pump.—A mercury pump is at times needed for the exhaustion of sample tubes like those described on page 4, and for the removal and collection of gases in certain operations such as those described on page 16. Of the many forms of mercury pumps that have been designed, that of Töpler is one of the most satisfactory. The construction and operation of this pump have been fully described by Travers.[15] He also gives a method for collecting the gases that are drawn from a container by the pump, but this has been found to be unsatisfactory and was later improved by Keyes.[16]

A simple and easily constructed form of Töpler pump that may be used if an efficient oil pump is not available has been designed by A. W. Laubengayer in the Cornell laboratory. The pump operates automatically and will reduce the pressure to about 0.005 mm. It does not, however, permit of the collection of the gas that is withdrawn.

[15] Travers, *Experimental Study of Gases* (1901), p. 6.
[16] *J. Am. Chem. Soc.*, **31**, 1271 (1909).

A (Fig. 9) is the barrel of the pump and is made of thick-walled glass tubing 5 cm. in diameter and 37 cm. long, constricted at each end, *H* and *K*. At *H* the barrel is joined to the vertical tube *C* which is connected to the tube *L* containing phosphorus pentoxide. The apparatus to be evacuated is attached to *N*. *B* is a heavy-wall pyrex flask of one liter capacity, joined to *C* by means of a rubber stopper. Inserted through this stopper is the tube *M* to which is attached a water suction-pump. The upper end of the barrel *A* terminates at *K* in the capillary delivery tube *D*. The lower end of *D* passes through a rubber stopper and dips into the mercury well *E*. *E* has two side-arms, *F* and *G*. *G* is 7 mm. in diameter, and is open at its upper end. It is connected to a second water suction-pump to hasten the preliminary evacuation. *F* is of capillary tubing, and connects the well *E* with the reservoir *B*.

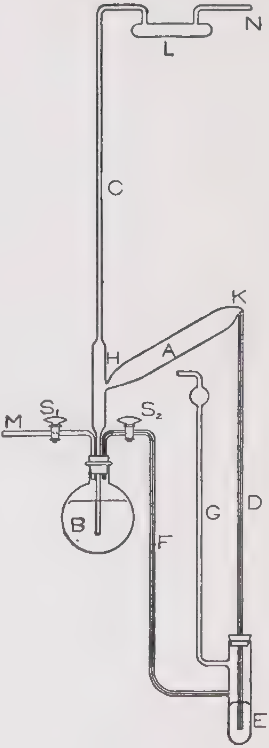

FIG. 9

In bringing the pump into operation stopcock S_2 is closed and S_1 is opened, and the water pumps attached to *M* and to *G* are started. This suction causes air to be withdrawn from the apparatus attached to *N* through *C*, and to bubble up through the mercury in *B*, passing out through S_1. When the pressure in *A* has thus been lowered as far as possible with the water pumps, the pump attached to *G* is disconnected and the stopcock S_2 is opened, whereupon air enters through *G*, passes into the flask *B* and through *F*, and causes the mercury to rise in

A. When the mercury reaches *H,* the air in *A,* which had been in equilibrium with the gas in the apparatus attached to *N,* is trapped and is expelled, as *A* fills, through the delivery tube *D* and through *F.* After filling the barrel *A,* the mercury passes down through the tube *D* and collects in *E.* The level of the mercury in *E* rises until it covers the opening to the tube *F,* whereupon mercury rises in *F.* This shuts off the supply of air to *B,* and allows the suction pump connected to *M* to lower the pressure in the reservoir *B* until the column of mercury in *C* and *A* is not sufficiently supported, whereupon it breaks at *K* and the mercury in *A* flows back into *B.* When the mercury falls below *H, A* is again connected to *C,* and the gas in it comes to equilibrium with the residual gas in the apparatus attached to *N.* During this interval, the pressure is being lowered in *B* by means of the water suction-pump until finally mercury is drawn from *E* through *F* to *B* and this continues until the mercury level in *E* falls below the opening of *F.* This opens *F* to the atmosphere, and the mercury in *B* is pushed up into *C* and *A,* trapping the gas in *A,* and the cycle already described is repeated. By means of stopcock S_2 the period of the pump may be controlled. After being started, the pump operates automatically.

A fairly accurate indication of the pressure in the apparatus may also be obtained with this pump. If the volume of *A* between *H* and *K,* and also the volume per linear centimeter of the tube *D* are known and the length of the bubble of gas in *D,* when it is near the bottom and at approximately atmospheric pressure, is observed, then from the two volumes and one pressure, the pressure in the apparatus may be calculated.

The exhaustion obtainable with a Töpler pump is not sufficient in many cases, and for investigations where very low pressures are essential, it is necessary to employ a mercury-vapor pump.[17]

A very simple arrangement that may be used for the exhaustion of apparatus and the removal and collection of gas consists of a mercury burette which has a double bore stopcock at the top. One tube from the stopcock connects to the apparatus to be evacuated: the other tube connects to another burette for the collection of the sample, or if the evacuated gas is not to be collected, the tube is left open to the air. The burette is connected to the apparatus to be evacuated and the mercury lowered by means of the levelling tube. The stopcock is then turned 180° and the gas is expelled or is forced into another burette for collecting the sample. This is repeated until all of the gas is removed.

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[17] Kaye, *High Vacua* (1927), p. 87; Peters, *Z. angew. Chem.,* **41**, 509 (1928).

Collection of Gases from Springs.—To collect gas from springs that are directly accessible, the small apparatus proposed by Bunsen[18] may be used (Fig. 10).

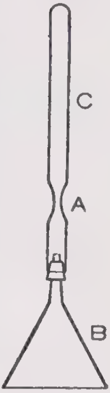

FIG. 10

This consists of a glass tube *C* of from 40 to 60 cc. capacity, drawn out at *A* before the blast-lamp to the size of a fine straw, and connected air-tight with the funnel *B* by means of a well-fitting cork or a piece of rubber tubing. The apparatus is filled with the water of the spring. This cannot be done without access of air, which would change the composition of the gases dissolved in the spring water in the tube. Hence the inverted apparatus, with the mouth of the funnel upward, is lowered below the level of the spring, and, with a narrow tube reaching to the bottom of the test tube, the water that in the first filling had come in contact with the air is sucked out until one is satisfied that it has been entirely replaced by other water from the spring. If now the gas of the spring is allowed to rise through the funnel into the test-tube thus filled, the purity of the sample is assured. If the rising bubbles stop in the neck of the funnel or at the contraction *A*, they can easily be made to ascend by tapping the edge of the funnel upon some hard substance. The apparatus is then placed in a small dish and removed from the spring, and the tube is sealed by fusion at *A*. This can easily be done with the blow-pipe, the moisture at the point *A* having first been driven away by warming.

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[18] Bunsen, *Gasometrische Methoden*, 2d. ed., p. 2.

Ramsay and Travers[19] have proposed an apparatus for collecting large quantities of gases from mineral waters in which a sampling tube, Fig. 4, can be used as shown in Fig. 11. The cylinder *A* is filled with the water of the spring, and the rising bubbles of gas pass into the cylinder through the funnel *D* and the tube *C*.

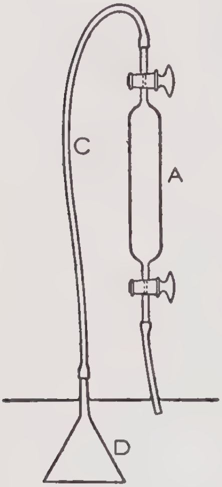

Fig. 11

More recently the apparatus shown in Fig. 12 has been suggested by Hackl.[20]

The entire apparatus is filled with water from the spring and is inverted under water over the spot where the gases escape. The rising bubbles of gas pass into the bottle through the funnel *B*, the water running out through *C*. After the sample is collected, the stopper with the funnel is removed and another containing two glass tubes closed with rubber tubes and pinchcocks is inserted. The bottle is then removed from the water, placed in an upright position and after connecting a funnel and burette to the two tubes, the gas can be transferred to the burette for analysis.

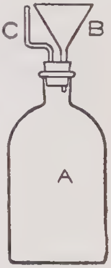

Fig. 12

Collection of Gases Dissolved in Liquids.—For the determination of the volume and composition of the dissolved gases in liquids, two groups of methods have been devised, those[21] which are based on the gas in solution taking part in a chemical reaction, and those [22] in which the gas is first removed from the water and then determined gasometrically. In the latter methods [23] the gases are first removed by heat or by pumping or by combination of both procedures; although accurate, they are not well adapted to general use because of the difficulty in removing the last traces of dissolved gases and in handling the removed gases. A very satisfactory method [24] is based upon the law of distribution of a gas between the liquid and vapor phases. In this case it is not necessary to remove all of the gas dissolved in the liquid in order to determine its amount. The liquid is brought into a vacuum and the system is brought to equilibrium by shaking. Then by the analysis of the gas phase and a knowledge of the temperature, volume, and the coefficients of distribution it is possible to calculate the amount of the gas in the two phases.

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[19] *Proc. Roy. Soc.*, London, **60**, 442 (1896).

[20] *Chem. Ztg.*, **43**, 421 (1919).

[21] Winkler, *Ber.*, **21**, 2843 (1888); **22**, 1764 (1889); Hale and Melia, *Ind. Eng. Chem.*, **5**, 976 (1913).

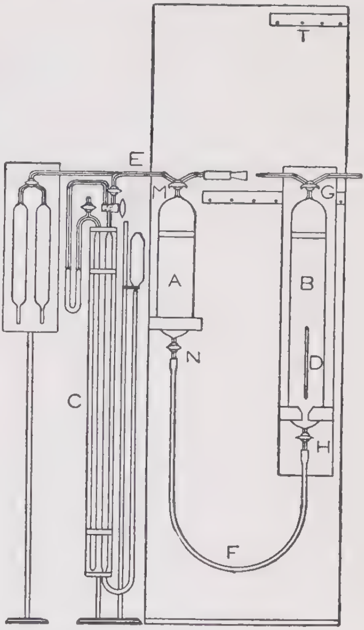

Fig. 13

The apparatus used by Swanson and Hulett is shown in Fig 13.

This consists of two cylindrical glass reservoirs *A* and *B* having a capacity of one-half liter and one liter respectively. They are fitted with "120 degree" three-way stopcocks at the upper ends and with straight stopcocks at the lower ends. A short range thermometer *D* is fastened to the inner wall of the cylinder *B* to determine the temperature of the contents accurately to 0.1°. The smaller cylinder *A* is filled with mercury and is permanently mounted to the frame. *B* can be moved horizontally or raised to the support *T*. *A* communicates with a gas burette *C* through the capillary tube *E*. The cylinders are connected at the bottom by a rubber tube *F*.

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[22] Tiemann and Preusse, *Ber.*, **12**, 1768 (1879); Hoppe-Seyler, *Z. anal. Chem.*, **31**, 367 (1892); Dennis, *Gas Analysis* (1913), p. 16.

[23] Lorah, Williams, and Thompson, *J. Am. Chem. Soc.*, **49**, 2991 (1927).

[24] Fresenius and Gruenhut, *Z. anal. Chem.*, **53**, 265 (1914); Swanson and Hulett, *J. Am. Chem. Soc.*, **37**, 2490 (1915).

The liquid to be examined is drawn directly into *B* and stopcocks *G* and *H* are closed to prevent a change in the amount of gas dissolved in the liquid. *B* is then placed on its carriage and joined to *A* by means of tube *F*, care being taken that there is no air enclosed in the connections. The stopcocks *N* and *H* are now opened and the mercury in *A* flows by gravity into the lower half of *B*, displacing an equal volume of water through stopcock *G*. Stopcock *G* is now closed, the carriage with *B* is raised to the support *T*, and the mercury is allowed to flow back into *A*, bringing the space above the water in *B* under diminished pressure. Stopcock *H* is then closed and *B* is removed from its support and is shaken vigorously for a few minutes in order to bring the liquid and vapor phases into equilibrium. *B* is now replaced in its carriage and is lowered to its original position, and stopcock *H* is opened. *B* is then moved to the left and is connected with *A* by the ground glass joint. Stopcocks *G* and *M* are then made communicating and the mercury from the burette *C* is driven over until it fills the line up to stopcock *G*. The stopcocks *M* and *G* are now so turned that *A* communicates with *B*, and the gas is transferred from *B* to *A* without change of pressure[25] because an equal volume of mercury flows from *A* to *B* through tube *F*. The gas can now be brought to any desired pressure over the mercury, and then transferred to the gas burette *C* and analyzed in the usual way.

From the amount of the gas found, the volume and temperature when in equilibrium with the water in bulb *B*, and the known [26] coefficients of distribution of the gases, the total amounts of the gas dissolved in the water can be calculated from the following formula,

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[25] It is not desirable to change the pressure of the gas while in contact with the water, as the amount remaining in solution will change.

$$x = \frac{a}{b} \quad \frac{bc(T + t)}{T} + d$$

in which

x = total number of cc. of the gas in the sample of liquid taken for analysis,

a = number of cc. of the gas actually removed,

b = volume of the liquid phase,

c = solubility coefficient of the gas at the temperature observed,

d = volume of the vapor phase,

T = absolute temperature,

t = observed temperature at which the gas and liquid phases were at equilibrium.

Swanson and Hulett [27] have also described a special apparatus of greater accuracy for the determination of dissolved oxygen.

Collection of Gases from Reactions in Sealed Tubes.—Gases are set free in many chemical reactions that take place in sealed tubes. If one wishes to examine these gases, Bunsen directs [28] that when the tube is fused together, it be drawn out to a fine tip about 2 mm. wide and 50 mm. long. To collect the gases given off, a mark is made at *A* (Fig. 14), with a sharp file, and the tip is connected with a capillary glass tube by means of a short piece of rubber tubing.

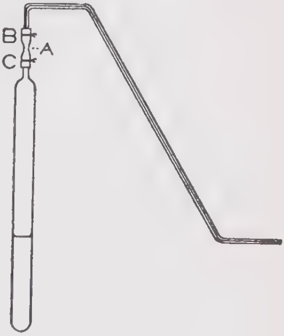

Fig. 14

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[26] Landolt-Börnstein, *Physikalisch Chemische Tabellen.*

[27] *Loc. cit.*

[28] Bunsen, *Gasometrische Methoden*, 2d ed., p. 10.

For safety's sake wire ligatures are put on at B and C. On breaking the tube inside the rubber at A, the gas passes through the delivery tube and can be collected in any desired receiver. If very strong pressure in the tube is to be expected, the rubber connection is surrounded with a strip of linen, and the tube itself is wrapped in a cloth. A third ligature put on at A makes it possible to stop the escape of gas at any time, the rubber forming with the broken-off glass tube a Bunsen rubber valve.

Extraction of Gases from Minerals.—For the extraction of gas present in minerals and rocks, Ramsay and Travers[29] have recommended that the mineral first be reduced to a fine powder and be then mixed with double its weight of primary potassium sulphate. The mixture is placed in a hard glass tube connected with an air-pump by means of a mercury seal. After the tube is exhausted, it is heated to redness with a large Bunsen burner. The escaping gases are pumped out and are collected in a small tube that contains a small amount of a solution of potassium hydroxide. Travers[30] has used somewhat similar tubes to collect the gases that are set free when minerals are heated in sealed tubes with sulphuric acid.

In a recent investigation Paneth[31] states that the gases present in a mineral are not driven out by heating the substance alone, and that it is necessary to bring the entire material into solution. He has described two forms of apparatus for the collection of small amounts of helium from iron and rock meteorites.

The form used for the solution of iron meteorites in the complete absence of air is shown in Fig. 15. About 5 grams of the material is introduced in A through E which is then sealed to the manometer. About 80 cc. of aqua regia is introduced into B through F, and the tube F is then sealed off. The bulbs A and B are each of about 150 cc. capacity. B is immersed in liquid air until the aqua regia is solidified, and then the entire apparatus is completely evacuated by joining it at *D* with the apparatus for the analysis of the gases, opening stopcocks *G, H,* and *I* and using the attached apparatus as a pump. To expel the air dissolved in the aqua regia, *A* is immersed in liquid air, stopcock *H* is closed and by continuing the pumping, the air is withdrawn and the aqua regia is distilled over into *A*. Stopcock *G* is now closed and the aqua regia allowed to melt, whereupon the material dissolves. During the solution *C* is immersed sufficiently in liquid air to condense the liberated nitric oxide and prevent the pressure from exceeding one atmosphere. After complete solution the nitric oxide in *C* is allowed to melt and the helium passes over into the space between *I* on the one side and *G* and *H* on the other, and stopcock *I* is closed. The gas is then transferred to the apparatus in which it is to be analyzed by washing out *A* and *B* many times with oxygen, which is then removed by absorption with charcoal.

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[29] *Proc. Roy. Soc.*, **60**, 442 (1896).
[30] *Proc. Roy. Soc.*, **64**, 132 (1898).
[31] *Z. Elektrochem.*, **34**, 645 (1928).

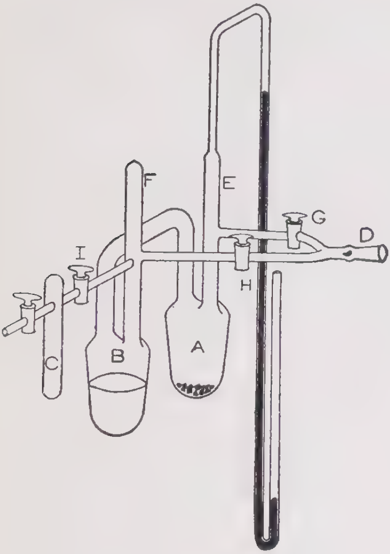

FIG. 15

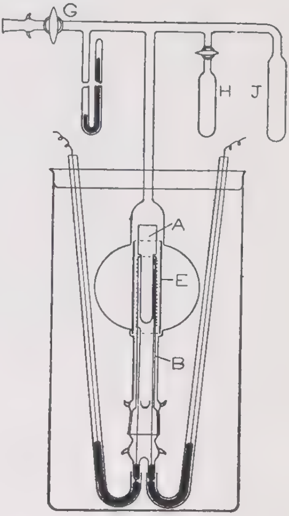

FIG. 16

Fig. 16 shows the apparatus that is used for the decomposition of rock in the absence of air. The rock, mixed with the decomposition material (sodium carbonate), is placed in the crucible *A* which rests upon the upper end of a clay tube *B*. The crucible is heated by a heating unit of chrome-nickel wire and to prevent radiation the crucible is surrounded by a glazed porcelain tube *E*. The entire apparatus is immersed in water. After the introduction of the mineral with the decomposition material into *A*, the entire apparatus is completely evacuated through G. Stopcock *G* is then closed and *H*, which is filled with a mixture of potassium dichromate and sodium carbonate, is gently heated until sufficient carbon dioxide is liberated to raise the pressure to about 300 mm. The crucible is then heated to a bright red heat, the pressure being regulated by the immersion of *J* in liquid air. The liberated gases are then transferred to the apparatus for the analysis in a manner similar to that described above.

Gasometers.—If a sample of gas is to be collected and kept for analysis for a considerable length of time, the portions of the gas taken for analysis must be displaced with mercury. Water may not be used for this purpose because its solvent power for gases would cause change in the composition of the gas mixture. A small gasometer that is suitable for prolonged storage of a gas sample is shown in Fig. 17. The large glass bulb *A* serves to hold the gas. At the top it carries the bent capillary tube *C*, and at the bottom it is joined to the level-bulb *B* by a rubber tube. The capillary is

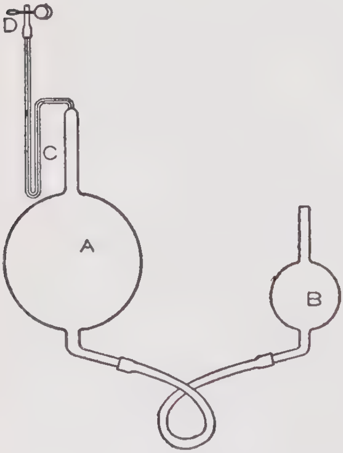

Fig. 17

closed by a rubber tube and pinchcock. The apparatus is first filled with mercury. By lowering or raising the level-bulb, gas can be drawn in or driven out as desired. If gases are to be kept for some time, the capillary tube *C* is filled with mercury by means of a little pipette inserted at *D*. This closes the bulb perfectly.

A convenient gasometer may easily be constructed from a round-bottomed flask fitted with a two-hole rubber stopper and bent glass tubes in the manner shown in Fig. 18. The thistle tube may be replaced by a level-bulb and rubber tube (see Fig. 17).

For the collection and storage of large samples of gas, gasometers as shown in Figs. 19 and 20 made of sheet iron or of glass[32] may be employed. The form shown in Fig. 19 may also be used instead of bottles (see p. 7) to aspirate the gas into the container. These large gasometers are not well adapted to the storage of gas samples for analysis because of the solvent action of water upon the constituents of the gas

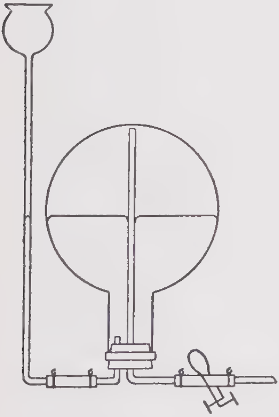

FIG. 18

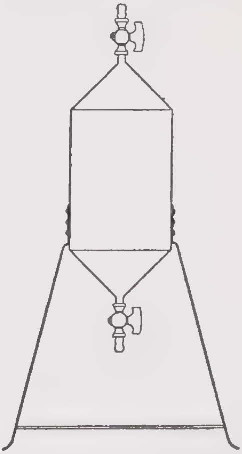

FIG. 19

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[32] Murmann, *Oesterr. Chem. Ztg.*, 17, 69 (1914), found that zinc cannot be used for containers of this kind as it combines with the carbon dioxide.

mixture. This defect may partially be remedied by using a concentrated solution of sodium chloride, of magnesium chloride, or glycerin as confining liquid.[33] The solvent action of the confining liquid may also be lessened by using a gasometer of such form as will give small surface of contact between the gas mixture and confining liquid[34] (see Fig. 21).

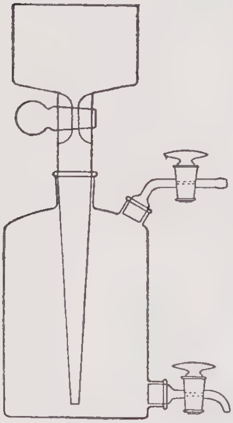

FIG. 20

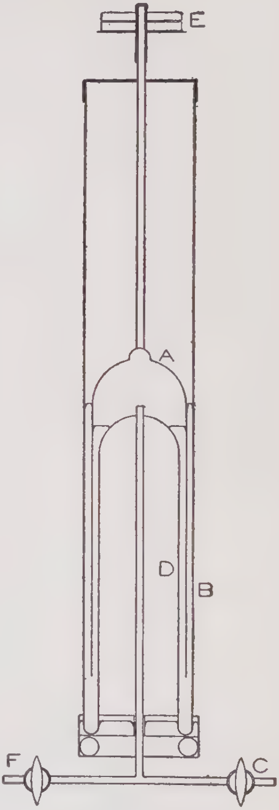

FIG. 21

The gasometer consists of the bell *A* which dips into the cylindrical ring-shaped space *B*, this latter being filled with a solution of magnesium chloride or with mercury. *D* is a hollow cylinder closed at both the top and bottom. The gasometer is filled by introducing the gas in question, through *C*. By means of the weight *E* it is possible to regulate at will the pressure in the gasometer. When the gasometer has been filled, the gas can be drawn off through the stopcock *F*. Similar gasometers are also made of glass. Modified forms[35] of gasometers have also been devised to deliver the gas at constant pressure.

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[33] See Gray, *J. Soc. Chem. Ind.*, **32**, 1092 (1913).
[34] Bodenstein, *Ber.*, **51**, 1640 (1918).
[35] Milbauer, *Z. anal. Chem.*, **57**, 161 (1918); *Chem. Ztg.*, **46**, 974 (1922).

CHAPTER II

THE MEASUREMENT OF LARGE SAMPLES OF GAS

When a gas is present in a gas mixture in only very small amounts, it is usually determined by drawing or forcing a large sample of the mixture through a suitable absorption apparatus, and ascertaining the amount of the absorbed constituent by gravimetric or volumetric means. It is evident that under such circumstances the large size of the gas sample obviates the necessity of very accurately determining its volume (see p. 118).

An arrangement of apparatus that is suitable for the approximate measurement of large gas volumes can easily be put together from stock apparatus in the laboratory. A large bottle is filled with water and is fitted with a stopper carrying an inlet tube and a siphon tube extending to the bottom of the bottle. The siphon tube is filled with water by blowing into the inlet tube and the pinchcock on the end of the siphon tube is closed. The inlet tube is then connected with the absorption apparatus (see Chap. XI) through which the sample is to be drawn and the pinchcock is opened. When the first bubble of gas passes through the absorbent, a graduated measuring cylinder is placed under the end of the siphon tube, and the water which runs out of the bottle is measured. After the operation is complete, the volume of gas represented by the water that has been measured in the cylinder is reduced to standard conditions and the percentage of the absorbed constituent in the original gas volume is then calculated.

Gas Meter.—A more convenient but more expensive apparatus for measuring large gas volumes is an Experimental Gas Meter of the type shown in Figs. 22 and 23. The meter is a "wet" meter and consists of a cylindrical casing of either monel metal, cast iron, steel, or brass, protected by a coating of tin, nickel, japan, or enamel. Enclosed in the casing is a rotating, horizontal drum made of some metal or alloy like tinned brass, German silver, or monel metal to withstand the

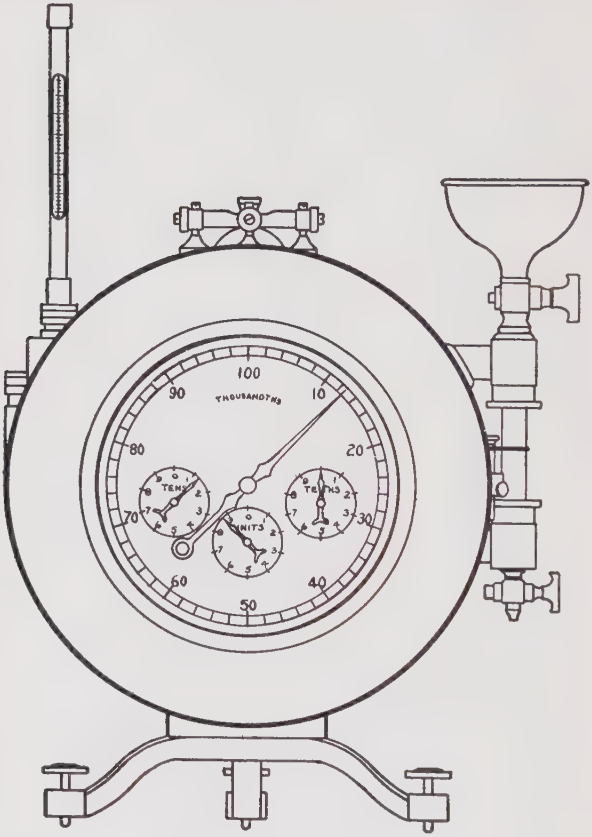

Fig. 22

corroding action of gases. The dials of the meters are so graduated that one complete revolution of the drum and the large pointer corresponds to one-tenth or one-twelfth cubic foot or to three liters, while the small pointers record the total volume of gas that has passed through the meter. The meter is also equipped with a level indicator, generally two spirit levels at right angles to each other, leveling screws at the base, a water-level indicator, and a thermometer.

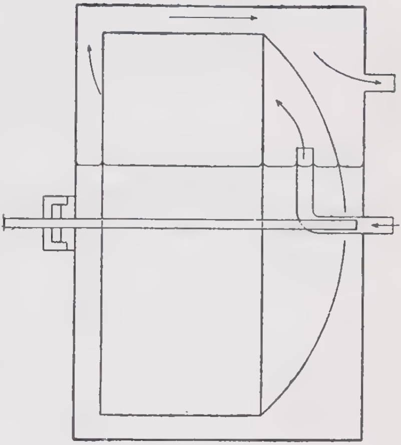

FIG. 23

The rotating drum is divided into four measuring compartments by partitions set at an angle favorable to their passage through the water, with the inlet and outlet openings at the back and front of the drum respectively. When one of these compartments is at its lowest point, both openings are under water and the compartment is filled with water. As the drum revolves, the opening at the rear emerges from the water, and the gas enters, the water escaping through the front opening. Due to the shape of the compartment, the pressure of the gas causes the drum to revolve until the compartment is nearly at the top position. The back opening then closes, momentarily sealing off a certain volume of gas. As the drum continues to revolve, the front opening emerges from the water, and the gas is forced out by the water entering the back opening until the compartment is again completely filled with water. Due to the use of four compartments, one is always discharging, and the rate of flow of the gas is almost constant. It can readily be seen from the above that the amount of gas delivered during each revolution will depend upon the volumes of gas sealed off in the compartments. This depends upon the level of the water; consequently a careful regulation of the height of the water is very important.

A meter of this type is prepared for use in the following manner. It is first set absolutely level by adjusting the leveling screws at the base, and is next filled with water until the water is slightly above the gauge mark. The meter is then connected with the gas supply, and gas is passed through it until the water is saturated with the gas. Both the inlet and outlet openings are disconnected and left open to the air, and the pointer is set at zero. The water-level is then adjusted exactly to the gauge mark, the meter is run through one more revolution, and the adjustment of the water-level is verified.

If the temperature, pressure, and humidity of the gas are known, the volume which has passed through the meter may be reduced to standard conditions.

An investigation [1] of the accuracy of wet gas meters has shown that they are influenced by various factors, and that it is necessary to calibrate these meters frequently to secure accurate results. This is done by passing a known volume of gas through the meter. The known volume of gas may most accurately be delivered from a standard bottle.[2] If this is not available, a previously standardized meter-prover or a gas container as shown in Fig. 19 may be used, or the method outlined on page 21 may be employed.

Walter and Marsh have described [3] a meter that will automatically make correction for varying conditions of temperature and pressure.

Dry Gas Meter.—In the study of gaseous metabolism there are certain objections inherent to the use of a wet meter. A suitable meter [4] for this purpose, and one that is, at the same time, both simple and inexpensive, may easily be adapted from the ordinary five-light, two-diaphragm, slide-valve consumers' meter shown in Fig. 24.

The meter has two soft, oiled leather bellows in closed compartments and it operates as a tandem reciprocating engine to rotate a vertical shaft that is connected to a dial which indicates the volume of gas passed per revolution. The leather diaphragms are the pistons mounted on the center division of the meter. When a diaphragm starts its outward stroke, the inside fills with gas and the diaphragm disc travels outward, causing a diminution of the gas space between the diaphragm and the outside confining walls of the meter. This diminution of space represents the gas displaced or delivered. When the diaphragm travels inward, the gas is flowing into the space between the outside of the case and the diaphragm. The diaphragm disc moving inward diminishes the volume within the diaphragm, which is the amount of gas delivered. A uniform rate of flow of gas is obtained by using two diaphragms; when one is at the end of its stroke the other is at the center of its stroke or point of maximum rate of delivery. The top of the meter may be removed and a graduated dial and hand may be placed on the vertical shaft as shown.

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[1] Waidner and Mueller, *Bureau of Standards, Tech. Paper* No. 36 (1914).

[2] *Bureau of Standards, Tech. Paper* No. 36 (1914); *Bureau of Standards, Tech. Paper* No. 114 (1919).

[3] *Gas World,* **66**, 129, 181 (1917).

[4] Newcomer, *J. Biol. Chem.,* **47**, 489 (1921).

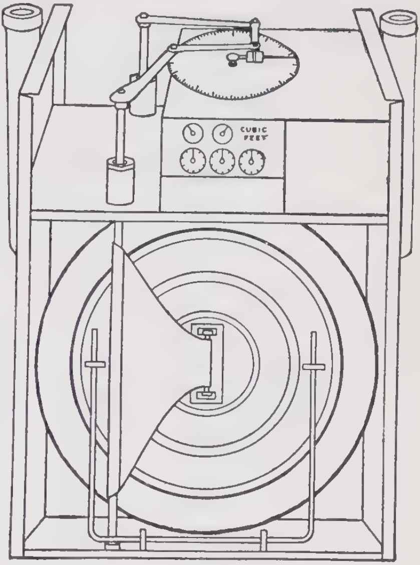

FIG. 24

The delivery of gas depends upon the proper timing of the valves and the stroke of the diaphragms. It has also been found[5] that the hand does not run evenly around the circle, and that it may vary as much as 180 cc. from the expected value. It will give consistent and accurate readings only for whole revolutions but not for fractions thereof. For this reason it is essential that such a meter be calibrated. This may be done by the methods outlined for the calibration of wet meters. Some method for determining the pressure, temperature, and humidity of the gas should also be provided.

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[5] Newcomer, *loc. cit.*; Krogh, *Biochem. J.*, **14**, 282 (1920).

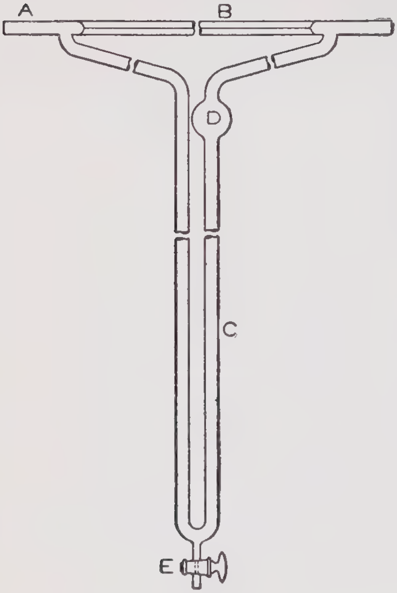

Fig. 25

Flow Meter.—In the measurement of small rates of flow, especially with corrosive gases, it has been found [6] that the customary methods of measuring the flow of a gas, *i.e.*, wet and dry meters, are unsuitable. Moreover they do not give an instantaneous reading of the rate of flow.

The measurement of small rates of flow can very satisfactorily be made with a resistance flow meter [7] of the type shown in Fig. 25.

The cross-section of the tube *A* through which the gas flows is partially closed by the insertion of a piece of capillary tubing *B* or by heating and drawing out the tube to form a construction. The two arms of a manometer *C*, which is filled with water or other convenient liquid, are connected to points on each side of the constriction in the manner shown. A large bulb *D* may be placed in the low pressure arm of the manometer to prevent the liquid being drawn into the tube A, and the refilling of the manometer is facilitated by a tube *E* sealed to the lower end of the manometer. When the gas flows, the manometer will show in the two arms a difference in level which is dependent upon the rate of flow. The drop in pressure can easily be measured by the use of a sliding scale which moves up and down between the arms of the manometer.

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[6] Benton, *Ind. Eng. Chem.*, **11**, 623 (1919).

[7] Ubbelohde and Hofsäss, *J. Gasbel.*, **55**, 557, 850 (1912); Hardebeck, *ibid.*, **55**, 849 (1912); Riesenfeld, *Chem. Ztg.*, **42**, 510 (1918); Benton, *loc. cit.;* Erlich, *Ann. chim. anal. chim. appl.*, **2**, 289 (1920); Yoe, *J. Soc. Chem. Ind.*, **44**, 432 (1925).

The flow meter is calibrated [8] for the particular gas to be measured, by determining the volume which passes through in a given time. This is done with previously calibrated wet or dry meters, and recording the pressure difference shown on the manometer. Then for a given flow meter a certain pressure difference will indicate the rate of flow. Automatic devices [9] may be used to maintain a constant head of pressure.

Other special devices such as the Pitot tube,[10] Venturi meter,[11] electric meter, [12] and orifice meter [13] may also be used. Bubble meters [14] and siphon meters [15] have also been suggested for the measurement of very small rates of gas flow.

Rotameter.—This instrument [16] is a unique and useful device for measuring the volume of gas per hour that is flowing through a tube. It consists of a vertical glass tube through which the gas passes in an upward direction. The diameter of the tube increases continuously from the bottom to the top and the speed of flow of the gas can be regulated by means of a stopcock at the bottom of the vertical tube. Inside the tube there is a little float which is carried upward by the flowing gas, and at the same time set in rapid rotation about its vertical axis by means of notches in its rim. The float will rise until it leaves enough space between itself and the tube for the gas to flow through with a drop in pressure equal to the weight of the float. The height of the float, which is measured by a scale attached to the tube, can be calibrated to show the volume of gas flowing through the tube per hour.

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[8] Obermiller, *Z. angew. Chem.*, **35**, 659 (1922).

[9] Joseph, *Chem. Abst.*, **10**, 708 (1916); Oberfell and Mase, *Ind. Eng. Chem.*, **11**, 294 (1919); Smith, *ibid.*, **16**, 22 (1924).

[10] Griggs, *J. Gas Lighting*, **120**, 670.

[11] *J. Gas Lighting*, **126**, 707; Wing, *J. Gas Lighting*, **129**, 526 (1915); *Der Apparatebau*, **36**, 214 (1924).

[12] *Z. angew. Chem.*, **32**, 222 (1919); *Gas. J.*, **151**, 76 (1920); Jefferson, *Gas Record*, **19**, No. 11, 31 (1921); *Gas Age-Record*, **48**, 594 (1921); Thomas, *J. Gas Lighting*, **121**, 186; Dunglinson, *Gas World*, **76**, No. 1955 (Coking and By-Products Sec.), 16 (1922).

[13] Hayward, *Chem. Met. Eng.*, **24**, 780 (1921); Knowland, *ibid.*, **24**, 956 (1921); Donaldson and McCollum, *ibid.*, **24**, 956 (1921); Pierce, Jones, Schelhardt, Peterson, *Oil and Gas J.*, **22**, No. 25, 82 (1923); Sharp, *Ind. Eng. Chem.*, **17**, 646 (1925).

[14] Burke, *Chem. News*, **117**, 368 (1918); Fuwa and Shattuck, *Ind. Eng. Chem.*, **15**, 230 (1923).

[15] Beckett, *J. Soc. Chem. Ind.*, **36**, 52 (1917).

[16] *Am. Gas Light J.*, **99**, 12.

CHAPTER III

THE REDUCTION OF A VOLUME OF GAS TO STANDARD CONDITIONS

The quantity of a gas may be determined either by measuring its volume, or by ascertaining its weight, or by causing it to enter into chemical reactions that render possible its determination by indirect gravimetric or volumetric methods. Because of the comparatively low densities of gases, the first method is usually most accurate as well as most convenient. In fact, in gas analytical work, the determination of the amount of a gas by direct measurement of its weight is but rarely employed.

For practical purposes it is sufficiently accurate to assume that every gas is a "perfect" gas, in which case the volume of the gas is affected by changes of pressure and temperature in the manner described below.

The Effect of Pressure.—The effect of pressure upon the volume of a gas is expressed in the law discovered in 1662 by Robert Boyle.

THE LAW OF BOYLE.—*Provided the temperature remains constant, the volume of a gas is inversely proportional to the pressure.*

$$v_0 : v = p : p_0$$

$$v_0 p_0 = vp. \tag{1}$$

The Effect of Temperature.—If a gas at 0° C. be warmed to 1° C. (the pressure remaining constant) it will expand $\frac{1}{273}$ of the volume that it occupied at 0°. If the temperature of the gas be raised from 0° to 273°, its volume will double. Similarly, if a gas be cooled below 0°, its volume will decrease $\frac{1}{273}$ of its volume at 0° for each degree of fall of temperature below 0°. These facts were discovered in 1787 by Charles.

THE LAW OF CHARLES.—*Provided the pressure remains constant, the volume of a gas is directly proportional to the absolute temperature: it will change* $\frac{1}{273}$, *or 0.00367,*[1] *of its volume at 0° for each degree change in temperature.*

$$v_0 : v = T_0 : T$$

$$\frac{v_0}{v} = \frac{T_0}{T} \qquad (2)$$

in which T represents the absolute temperature.

Furthermore, if the volume of a gas remains constant, its pressure is directly proportional to the absolute temperature. It will change $\frac{1}{273}$ or 0.00367 of its pressure at 0° for each degree of change in temperature.

$$p_0 : p = T_0 : T$$

$$\frac{p_0}{p} = \frac{T_0}{T} \qquad (3)$$

We have seen by equation (1) that the product of the pressure and volume at constant temperature is a constant. Also from equation (2) that the volume is directly proportional to the absolute temperature at constant pressure. It is convenient to combine these statements into a single expression.

If p_0v_0 be the pressure and volume of a gas at T_0 (standard conditions) and pv the pressure and volume at T, then if the pressure is changed from p_0 to p with the temperature constant at T_0, the volume will change to an intermediate volume v_1. Then from equation (1),

$$v_0 : v_1 = p : p_0$$

or

$$v_1 = \frac{p_0v_0}{p} \qquad (4)$$

If the temperature changes from T_0 to T, the pressure remaining constant at p, then applying equation (2),

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[1] The correct value of $\frac{1}{273}$ is 0.003663, but 0.00367 is more nearly the average for ordinary "permanent" gases.

$$v_1 : v = T_0 : T$$

$$v_1 = \frac{vT_0}{T} \tag{5}$$

Combining (4) and (5),

$$\frac{vT_0}{T} = \frac{p_0v_0}{p_0T}$$

or

$$v_0 = v\frac{pT_0}{p_0T} \tag{6}$$

But $p_0 = 760$ mm., and $T_0 = 0°$ C. (273° absolute temperature). Consequently

$$\frac{T_0}{T} = \frac{273}{273 + t} \quad \text{or} \quad \frac{1}{1 + 1/273t} \quad \text{or} \quad \frac{1}{1 + 0.00367t}$$[2]

If v_0 is the volume under standard conditions, v the observed volume, p the observed pressure expressed in millimeters of mercury, and t the observed temperature in degrees Centigrade, then substituting these values in equation (6),

$$v_0 = v\frac{p}{760(1 + 0.00367t)} \tag{7}$$

Instead of the value 0.00367, the actual values of the coefficient of expansion of the different gases are used in very accurate work. These are given in Table I.

TABLE I

COEFFICIENTS OF EXPANSION

Air	.003669	NH_3	.00386
N_2	.003673	NO	.00368
H_2	.003661	HCl	.00374
CO	.003665	C_2H_4	.00374
CO_2	.003729 to .003737	O_2	.00368
N_2O	.003729	H_2S	.00377
CN	.00388	Cl	.00383
SO_2	.00398	C_2H_6	.00377
C_2H_2	.00374	CH_4	.00368

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[2] The values for this expression are given in the table on page 467.

In stating the volume of a gas it is agreed among scientists to express it in terms of the volume that the gas would occupy under certain arbitrary (standard) conditions, that is at a temperature of 0° C., and under a pressure of 760 mm. of mercury, and free from moisture.

By means of the above formula (7), a gas volume may correctly be reduced to standard conditions provided the gas, when measured, contains no water vapor. If, however, water vapor is present, a correction must be introduced. Every liquid tends to change to the gaseous state, and the vapor of the liquid exerts a gas pressure which is termed the vapor pressure of the liquid. This vapor pressure is dependent upon the temperature and upon the nature of the liquid, but it is not affected by the pressure of other gases, nor by the amount of the liquid that is present. If a closed space is filled with a mixture of gases, each gas will exert a definite pressure which is the same whether it exists alone in the space or whether other gases are present. The total pressure of the gas mixture is the sum of the partial pressures of the various gases. If now a gas volume that contains water vapor is measured at atmospheric pressure, the partial pressure of the dry gas will equal the barometric pressure less the pressure of the water vapor in the gas. If the gas is not "saturated" with water vapor, the partial pressure of the latter is difficult to determine. But when a gas is measured over water, or over mercury upon which stands a small amount of water, the space is saturated with water vapor, and since the maximum pressure of water vapor at various temperatures is known (see table on p. 471) the pressure of the dry gas can easily be ascertained by noting the temperature of the gas and subtracting from the observed barometric pressure the pressure of water vapor at the observed temperature. Representing the pressure of the water vapor by m, and inserting this correction in formula (7), we obtain

$$v_0 = v\frac{p - m}{760(1 + 0.00367t)} \qquad (8)$$

Inasmuch as the vapor pressures of liquids vary with the nature of the liquids, it is apparent that if a gas is measured over a liquid other than pure water, the correction to be introduced for the vapor pressure of the liquid will not be the same as for that of pure water. For this reason those forms of apparatus in which gas volumes are measured over concentrated solutions of various absorbents will not yield accurate results unless the vapor pressure of each solution is known and taken into account. To avoid error from this source it is customary, in the better types of apparatus, to pass the gas mixture from a measuring burette into a separate apparatus containing the absorbent, and to then draw the gas back into a gas burette where it comes into contact with water before being again measured. In this manner the space occupied by the gas is always saturated with water vapor when the volume of the gas is measured.

When a gas is measured over dry mercury, the vapor pressure of the mercury is so small as to be negligible unless the gas is measured at a temperature considerably above 40°.

BAROMETRY

As previously stated, it is customary to express the volume of a gas in terms of the volume that it would occupy under standard conditions. If the gas is measured under atmospheric pressure, that pressure must be determined before the reduction of the gas volume can be made. The standard pressure has been taken as the mean pressure at sea-level and at a latitude of 45°, which has been found to be 762.703 mm. or 30.028 inches of mercury. For scientific purposes, however, the standard pressure is taken as 760 mm. or 29.921 inches of mercury.

The pressure of the atmosphere is not constant. It is measured by a barometer, of which there are two types, the aneroid and the mercurial.

The Aneroid Barometer.—The aneroid barometer consists of a circular vacuum chamber with a thin, corrugated, metallic cover. Changes in the pressure of the air cause a change in the curvature of the cover, and this movement is transmitted to a pointer. This type of instrument is less accurate than the mercurial barometer, and it is not used for scientific work although widely employed where a portable, direct-reading instrument is desired.

The Mercurial Barometer.—The mercurial barometer is an upright tube which is closed at the top and which contains mercury, but no air above the mercury. It is fitted with a scale and vernier for accurately measuring the height of the mercury column which varies with the pressure of the atmosphere. The cistern *A* (Fig. 26) has a leather bottom, the center of which rests on the screw *C*. By turning the nut, the level of the mercury in the cistern can be raised or lowered until it is just in contact with the end of the ivory pointer *D*.[3] By this method the level of the mercury in the cistern is always at the zero of the scale on which the height of the mercury is read.

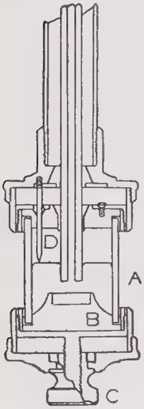

FIG. 26

In the improved form of this barometer shown in the figure, the cistern consists of a heavy-walled cylinder *A* which is securely held in position in a revolving frame. The bottom of the frame *B* is connected with the threaded stem and the nut *C*.

Correction of Barometric Readings.—Assuming the barometer to be correctly filled and in perfect adjustment, corrections should still be applied to reduce the observed reading to what it would be if the acceleration of gravity were a standard value, if the mercury and scale were at standard temperature, and if capillary depression had no effect upon the height of the column of mercury. The reasons and the methods for making these corrections are given below.

CORRECTION FOR GRAVITY.—For a column of any material, the total force F exerted on the supporting medium is equal to the product of the mass M of the material, times the acceleration g due to gravity, or

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[3] Stillman, *Bureau of Standards, Sci. Paper* No. 214 (1914).

$$F = g \times M,$$

and since the mass is equal to the product of the density d times the volume V, then

$$F = g \times d \times V.$$

If the column is of uniform cross-section, the volume is equal to the product of the height h times the cross-sectional area A, or

$$V = h \times A.$$

Then

$$F = g \times d \times h \times A.$$

The pressure is the force acting upon a unit area which, in absolute units, is dynes per square centimeter. Therefore the pressure P is

$$P = \frac{F}{A} = \frac{g \times d \times h \times A}{A} = g \times d \times h.$$

In barometry the absolute pressure is not used, but the height of the column of mercury is taken as a measure of the pressure. For this to be true, the product of the acceleration of gravity and the density must be a constant, or

$$h = \frac{P}{g \times d} = KP.$$

As a standard of reference, the value of g is taken as that at sea-level and 45° latitude, and d as the density at 0° C. For any pressure P dynes per square centimeter at 45° latitude, at sea-level and 0° C.

$$P = g_{45} \times d_0 \times h_0.$$

At any other latitude where the acceleration due to gravity is g_1, and at a temperature where the density is d_1, the pressure will be

$$P = g_1 \times d_1 \times h_1.$$

Then

$$g_{45} \times d_0 \times h_0 = g_1 \times d_1 \times h_1$$

or

$$\therefore \quad h_0 = h_1 \frac{g_1}{g_{45}} \times \frac{d_1}{d_0}.$$

The ratio g_1/g_{45} may readily be determined if the value of g_1 is known, because g_{45} is 980.665 cm. per second per second.

The value of g_1 may be calculated from the equation

$$g_1 = 980.665(1 - 0.0026 \cos 2\phi - 0.0000002H)$$

where ϕ is the latitude and H is the height above sea-level in meters.

The ratio d_1/d_0 may be determined from the expression

$$\frac{d_1}{d_0} = \frac{V_0}{V_1}$$

since

$$d_0 = \frac{M}{V_0}, \qquad \text{and} \qquad d_1 = \frac{M}{V_1}.$$

CORRECTION FOR THE TEMPERATURE OF THE MERCURY.—If β is the coefficient of cubical expansion of mercury, *i.e.* the change in volume per unit volume per degree change in temperature, then

$$V_0 = V_1(1 - \beta)^t$$

and

$$(1 - \beta)^t = 1 - \beta t + \frac{t(t - 1)\beta^2}{2}, \text{ etc.}$$

But since β is very small (181.8×10^{-6} per °C.), the terms with powers greater than one may be disregarded without appreciably influencing the accuracy. Hence we can say that

$$V_0 = V_1(1 - \beta t).$$

Then

$$\frac{d_1}{d_0} = \frac{V_0}{V_1} = \frac{V_1(1 - \beta t)}{V_1} = \frac{1 - \beta t}{1}$$

or

$$h_0 = h_1(1 - \beta t)\frac{g_1}{g_{45}} \cdot$$

CORRECTION FOR THE MEASURED HEIGHT OF THE MERCURY COLUMN.—Only under certain conditions will the true height of the mercury column be equal to the measured height. The factors which influence this are (1) the expansion of the scale, (2) the vapor pressure of mercury, and (3) the capillary depression.

Expansion of the Scale.—The scale that is used for measuring the height of the column of mercury should be so adjusted that the scale reading of the difference in level of the two surfaces of mercury is given correctly at any temperature at which the reading is made. That is, the zero point on the scale, if the scale is imagined to be continued downward, should always coincide with the tip of the ivory adjustment pointer. However, the scale will increase in length with rise of temperature, and since the scale is so graduated that the divisions on the scale are true millimeters only at 0° C., the measured height will not be the true height unless the scale is used at 0°. If the measurement is made at a temperature above 0°, then the measured height will be too small because of the lengthening of the scale. Therefore

$$h_1 = h[1 + \alpha\ (t - t_s)]$$

in which h is the measured height, t is the temperature of measurement, t_s is the temperature at which the scale reads correctly, and α is the coefficient of linear expansion of the material on which the scale is engraved. The scale is usually made of brass for which $\alpha = 18.4 \times 10^{-6}$ per °C. For glass, $\alpha = 8.5 \times 10^{-6}$ per °C.

The corrections for a scale graduated in millimeters are made to 0° C. for both the scale and the mercury. With a scale graduated in inches, the corrections are similar except that the readings are corrected to 32° F. for the mercury and 62° F. for the scale. This difference is due to the definitions of the meter and the British yard. On barometers equipped with combination scales, each scale should conform to its own specifications.

Vapor Pressure of Mercury.—There will always be vapor of mercury in the free space above the mercury in the barometer tube. The pressure of this vapor will depend upon the temperature, and will lower the height of the mercury column. Therefore the correction for the vapor pressure of the mercury should be added to the height of the mercury column.

The vapor pressure of mercury at different temperatures is given in Table II.[4]

TABLE II

Temperature ° C.	Vapor Pressure mm.	Temperature ° C.	Vapor Pressure mm.
0	0.0002	24	0.0018
10	0.0005	26	0.0022
16	0.0009	28	0.0025
18	0.0011	30	0.0030
20	0.0013	34	0.0041
22	0.0016	40	0.0065

Capillary Depression.[5]—When a glass tube (Fig. 27) of small internal diameter, and open at both ends, is placed in a vertical position with its lower end in a vessel of water, the surface of the liquid in the tube is higher than the surface in the vessel. This elevation is due to capillarity.

The water in the tube meets the walls of the tube in a circle of radius r equal to the radius of the circular bore, and at every point of the circle the angle of contact is the angle of capillarity β.

The amount of pull per unit length of the circumference, or the surface tension, is ρ and the component of this force parallel to the tube is $\rho \cos \beta$. For the entire circumference, this upward force is equal to $2\pi r\, \rho \cos \beta$. This raising force, due to surface tension, will raise the liquid until the downward pull of gravity equals the supporting force, when

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[4] Landolt-Börnstein, *Physikalisch-Chemische Tabellen.*

[5] The authors are indebted to H. H. Kimball and E. W. Woolard of the United States Weather Bureau for this explanation.

$$2\pi r\rho \cos \beta = \pi r^2 hdg.$$

If the small tube is placed upright coaxially with a larger circular cylinder, the real ascension h in the small tube will be equal to the apparent ascension H in the small tube plus the ascension h′ in the annular space (Fig. 28).

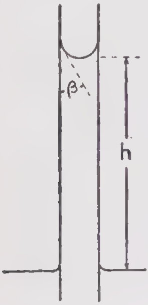

FIG. 27

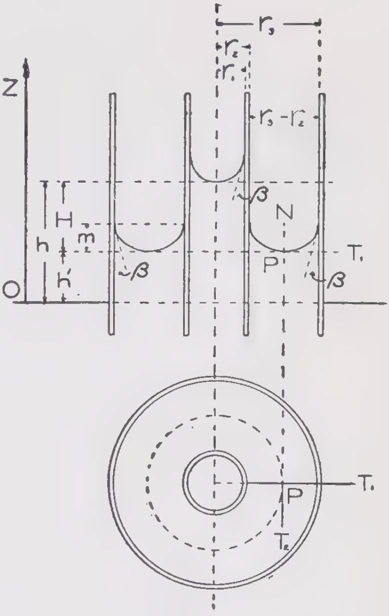

FIG. 28

Then in the small tube of radius r_1

$$2\pi r_1\rho \cos \beta = \pi r_1^2 hdg$$

and

$$h = \frac{2\rho \cos \beta}{r_1 dg}.$$

If we apply the same relations to the annular space of radius $(r_3 - r_2)$,

$$2\pi(r_3 + r_2)\rho \cos \beta = \pi(r_3^2 - r_2^2)h'dg$$

and

$$h' = \frac{2\rho \cos \beta}{(r_3 - r_2)dg}.$$

Hence

$$\frac{h'}{h} = \frac{r'}{r_3 - r_2}.$$

These relations are based on the assumption that the angle of contact β is constant, and the quantity of liquid raised against the walls above the horizontal plane tangent to the meniscus is negligible, or that the meridian (radial) section of the meniscus is circular. Both assumptions are fairly accurate in a narrow cylindrical tube.

However, in the rather wide annular space it cannot be assumed either that the quantity of the liquid raised against the walls is negligible or that the meridian section of the surface is a circle. Vershaffelt[6] has assumed that the meridian section of the surface in the annular space is nearly an ellipse with a semi-major axis of $(r_3 - r_2)/2$ and a semi-minor axis of m, where m is the depth of the annular meniscus. This is purely a gratuitous assumption for which there is no justification except that it is in close agreement with observation, at least under the proper conditions.

The curvature of the liquid surface introduces a pressure $\rho\ (1/R_1 + 1/R_2)$ directed toward the center of the surface,[7] in which R_1 and R_2 are the principal radii of curvature.[8]

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[6] *Comm. Phys. Lab. Univ. Leiden*, **32.**

[7] Gray, *Treatise on Physics*, Vol. 1, London (1901), pp. 642–643; Christiansen, *Elements of Theoretical Physics* (trans. by Magie), London (1897), pp. 122–123.

[8] The plane tangent to a curved surface at a given point contains the tangents to all the curves drawn on the surface through that point. The normal to this plane is the normal to the surface at that point. An infinite number of planes may be passed through the tangent to any curve on the surface at a given point, and the one which also passes through the normal intersects the surface in a curve called the normal section in the direction of the curve. There is an infinite number of these normal sections at the point of the normal, one in each direction. At every non-singular point of a surface there is one direction for which the radius of curvature of the normal section is a maximum. There is also one for which it is a minimum, and it has been shown that these two directions are at right angles to each other. These two extreme

Hence if we balance this upward force against the downward pull of gravity at any point of the meniscus, we obtain per unit area at this point, for any elevation z,

$$\rho\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=gdz. \tag{1}$$

Substituting in this equation the conditions existing in the inner tube where the two principal radii of curvature are the same [9] or the surface is assumed to be spherical, and $\beta = 0$,

$$\frac{2\rho}{r_1}=ghd=gd(H+h').$$

The bottom of the meniscus in the annular space is a circle of radius

$$r=r_2+\left(\frac{r_3-r_2}{2}\right)$$

lying in a plane. Hence from Meusnier's Theorem, the radius of curvature of the surface of the meniscus at a point P at the bottom in the direction PT_2 is infinite, or $R_2 = \infty$. Since ∞ is obviously a maximum, it is one of the principal radii of curvature, and the other R_1 in the direction PT_1 will be [10] the radius of curvature at P of the elliptical cross-section of the meniscus or

$$\frac{\left(\frac{r_3-r_2}{2}\right)^2}{m}$$

Then substituting these values in equation 1,

$$\frac{\rho m}{\frac{1}{4}(r_3-r_2)^2}=gdh'$$

---

radii of curvature are known as the principal radii of curvature at the point. They are equal to each other for a sphere or a plane, but in no other case.

[9] Gray, *op. cit.*, pp. 648–649.

[10] See Osgood, *Introduction to Calculus*, p. 260; Wilson, *Advanced Calculus*, pp. 143–145; Eisenhart, *Differential Geometry*, pp. 117–119, 123–124; Bell, *Coördinate Geometry of Three Dimensions.*

whence

$$\frac{h'}{H} = \frac{2m}{\frac{(r_3 - r_2)^2}{r_1} - 2m} \qquad \text{or} \qquad \frac{h'}{h} = \frac{2mr_1}{(r_3 - r_2)^2}$$

and

$$h' = \frac{2mhr_1}{(r_3 - r_2)^2}$$

where

h' = the depression in the annular space,
m = the depth of the annular meniscus,
r_1 = the interior radius of the small tube,
r_2 = the exterior radius of the small tube,
r_3 = the interior radius of the cistern,
h = the depression in the small tube which is obtained from the following table:

TABLE III

CAPILLARY DEPRESSION OF THE APEX OF A MERCURIAL COLUMN IN A GLASS TUBE OF CIRCULAR SECTION[11]

Depression in Millimeters

RADIUS OF THE TUBE (mm.)	HEIGHT OF THE MENISCUS (mm.)								
	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
1.0	2.46	4.40							
1.4	1.26	2.36	3.22						
1.8	0.75	1.44	2.02	2.48					
2.2	0.49	0.95	1.36	1.70	1.98				
2.6	0.34	0.66	0.96	1.22	1.44	1.61			
3.0	0.24	0.48	0.70	0.90	1.07	1.21	1.32		
3.5	0.17	0.34	0.49	0.64	0.76	0.87	0.96	1.04	
4.0	0.12	0.24	0.35	0.46	0.56	0.64	0.71	0.77	0.82
4.5	0.09	0.18	0.26	0.34	0.41	0.47	0.53	0.58	0.62
5.0	0.07	0.13	0.19	0.25	0.30	0.35	0.40	0.44	0.47
5.5	0.05	0.10	0.14	0.19	0.23	0.27	0.30	0.33	0.36
6.0	0.04	0.07	0.11	0.14	0.18	0.20	0.23	0.25	0.27
6.5	0.03	0.06	0.09	0.11	0.14	0.16	0.18	0.20	0.21
7.0	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.15	0.16

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[11] *International Critical Tables,* Vol. 1, p. 70.

In the case of mercury there will be a depression instead of an elevation, but according to Laplace the equations are the same for a convex meniscus as those for a concave one except for sign. Therefore the depression correction H in a cistern barometer is

$$H = h - h'$$

COMPLETE CORRECTION OF BAROMETRIC READINGS.—The total correction is given by the expression

$$h_0 = (h[1 + \alpha(t - t_s)] + V_p + C_d)(1 - \beta t)\frac{g_1}{g_{45}}$$

in which

h = measured height of barometer,
α = coefficient of linear expansion of the scale (brass = 18.4×10^{-6} per °C.; glass = 8.5×10^{-6} per °C.),
t = temperature of reading °C.,
t_s = temperature at which the scale reads correctly,
V_p = vapor pressure of mercury at the temperature t,
C_d = capillary depression,
β = coefficient of cubical expansion of mercury (181.8×10^{-6} per °C.),
g_1 = acceleration of gravity at place of reading,
g_{45} = acceleration of gravity at 45° latitude and sea-level (980.665 cm. sec.$^{-2}$).

RESIDUAL GAS ERROR.—In addition to the above errors of reading, there is liable to be an error due to the residual gas in the barometer tube, which may have been introduced during shipment or handling. The magnitude of this error will increase as the mercury approaches the top of the tube and with increase in temperature. This correction is determined[12] by forcing the mercury toward the top of the tube and comparing the height of the mercury point by point with an auxiliary barometer. In most barometers this error[13] does

[12] *Bureau of Standards Circular* No. 46 (1922).
[13] *International Critical Tables*, Vol. I, p. 70.

not exceed 0.25 mm. when the instrument is shipped by the manufacturer.

MANOMETRY

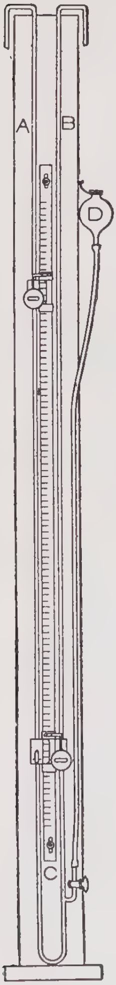

Fig. 29

The pressure of a gas in an enclosed system is usually measured by a simple manometer as shown in Fig. 29. This consists essentially of a glass U-tube provided with a scale. The tube *A* is connected to the apparatus, and the pressure is determined by the difference of the mercury level in tubes *A* and *B* which is read on scale *C*. The amount of the mercury in *A* and *B* is adjusted by means of the level-bulb *D*. The reading of the manometer may then be corrected for capillarity, gravity, and thermal expansion of the mercury and the scale, as described in the preceding pages.

Many investigators[14] have so modified this apparatus as to make it possible to measure the pressure of gases that would attack mercury.

Germann[15] has described a precision manometer, Fig. 30, for the accurate measurement of pressure.

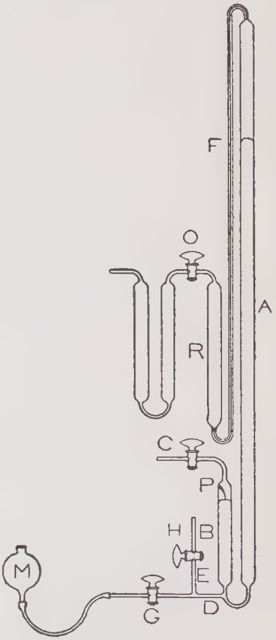

Fig. 30

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[14] Smith and Taylor, *J. Am. Chem. Soc.*, **46**, 1393 (1924); Klemenc, *ibid.*, **47**, 2173 (1925); Daniels, *ibid.*, **50**, 1115 (1928).

[15] *J. Am. Chem. Soc.*, **36**, 2456 (1914).

It consists of two tubes *A* and *B* of the same diameter connected at the bottom by a narrow U-tube. The short tube *B*, about 20 cm. long, has a colored glass point *P* sealed into it, to which the lower mercury level is adjusted in making a reading. The connection to the apparatus in which the gas pressure is to be measured is made through *C*. Sealed into the U-tube at *D* is a T-tube having two stopcocks *G* and *H*. Any air admitted with the mercury collects in *E* and is expelled through *H*. The other tube *A*, about 110 cm. long, terminates in a 0.2 mm. capillary tube *F* about 76 cm. long. The lower end of *F* is bent upwards and joins the large tube *R*, which is connected to a water pump through *O* and the two drying tubes containing calcium chloride and phosphorus pentoxide.

After thoroughly cleaning and drying the manometer, the stopcocks *H* and *C* are closed, and freshly distilled mercury is run in from *M* by applying a gentle suction through *O*. The mercury is admitted until it completely fills *A* and runs over into *R*. *M* is then lowered and the mercury in *A* falls to the point at which it is in equilibrium with the air in *B*. The pressure of the gas may be determined from the height of the mercury in *A* after opening *C* and adjusting the height of the mercury in *B* to the point *P* by means of the level bulb *M*. The reading is then corrected for capillarity, gravity, and thermal expansion of mercury and the scale, as described on the preceding pages.

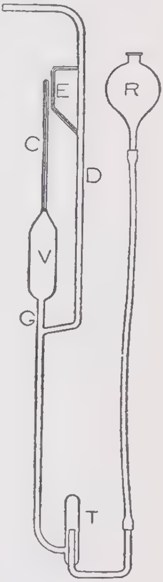

FIG. 31

McLeod Gauge.—The measurement of the pressure of rarefied gases is generally made by means of the instrument designed by McLeod, although the accuracy [16] of the apparatus has been questioned.

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[16] Ramsay and Baly, *Phil. Mag.*, (5) **38**, 301 (1894).

The instrument (Fig. 31) consists of a cylinder *V* which terminates in a closed capillary tube *C* and is connected with the exhausted apparatus through the tube *D*. It is joined to a mercury reservoir *R* through the trap *T* which collects any entrained air from *R*.

The volume of the cylinder *V* and the total volume and the volume per division of the graduated capillary tube *C* must be accurately ascertained.

In making a reading, the reservoir is raised until the mercury in the comparison capillary *E* has risen to the height of the top of the capillary tube *C*. The difference in height of the two mercury columns and the volume of the gas in *C* are then read.

The measurement of the pressure with this instrument is based on the assumption that the law

$$PV = pv$$

is valid over wide differences of pressure. Then if P is the pressure which is to be determined, which is the same as that in the apparatus when the mercury level is below *G*,

$$P = \frac{pv}{V}$$

in which

V = volume of $V + C$,

p = pressure at the time of reading,

which is the barometric pressure plus the difference in height in the two capillary tubes, and

v = volume in C.

The range of this instrument may be increased by a bulb blown in *C*,[17] or by having detachable compression chambers of various sizes [18] which are connected at *G* by a ground-glass joint with a mercury seal, or by measuring the pressure in the capillary with a hot-wire gauge.[19] Bailey's modification avoids the use of rubber connections, and he prevents the too rapid rise of mercury in the compression chamber by governing the rate of flow with a small opening in a tube above the reservoir. Harrington[20] uses a float in the mercury reservoir for this same purpose.

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[17] Duffendack and Schaefer, *J. Optical Soc. Am.*, **9**, 689 (1924).

[18] Bailey, *Chem. News*, **120**, 302 (1920).

[19] Pfund, *Phys. Rev.*, **18**, 78 (1921).

A small and very convenient form of the McLeod gauge, which is about twenty-four inches high, is shown in Fig. 32.[21]

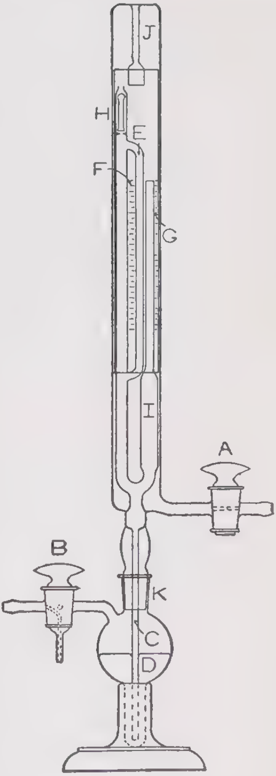

FIG. 32

The gauge is sealed inside of the large tube *J*. Both the inside and the outside of the gauge tubes and the reservoir *D* are evacuated at the same time through the stopcocks *A* and *B*. *A* is connected to the apparatus in which the pressure is to be measured and *B* is connected to a water suction-pump. This evacuation is carried out with careful manipulation of both stopcocks until with both fully opened the mercury stands in tube *C* somewhere below the ground-glass joint *K* at the top of the mercury reservoir *D*. Stopcock *B* is then slowly turned to connect *D* with the atmosphere and the mercury is carefully allowed to rise in tube *E* exactly to the zero mark on the scale *F* which corresponds to the top of tube *I*. The valve *H* is to prevent the mercury from flowing out of the tube in case *B* is opened too rapidly. The pressure is now read from the position of the mercury in tube *I* on the calibrated scale *G* in case it coincides exactly with one of the marked graduations. Otherwise the pressure is calculated

[20] *J. Optical Soc. Am.*, **9**, 469 (1924).
[21] Made by Hanff and Buest, Berlin.

from the reading of the height of the mercury in *I* on the millimeter scale *F* where the pressure P is

$$P = a^2 \times 10^{-3} + 11a^3 \times 10^{-7} \text{ mm.}$$

in which a is the reading on scale *F*. After use, the mercury is drawn down into *C*, both stopcocks are closed, and the gauge is allowed to stand evacuated. The suction pump attached to *B* is run continuously while making a reading to enable the mercury to be drawn down in case it rises above the zero mark in tube *E*.

Burk[22] has described a gauge combining the principle of the McLeod gauge and the quartz fiber manometer for the measurement of very low pressures.

[22] *J. Phys. Chem.*, **31**, 591 (1927).

CHAPTER IV

THE DETERMINATION OF THE DENSITY AND THE SPECIFIC GRAVITY OF GASES

The density of a gas is the mass of a unit volume measured under specific conditions of temperature and pressure, which usually are at the melting point of pure ice, under a pressure equivalent to 760 mm. of mercury at sea-level in the latitude of Paris. The specific gravity is the ratio of the weight of a given volume of the dry gas to the weight of an equal volume of dry, pure air, at the same temperature and pressure. Comparisons are sometimes made when both the gas and air are saturated with water vapor, but under these conditions the values may be quite different from those for the dry gases.

DETERMINATION OF THE DENSITY OF A GAS

The density is usually determined by direct weighing. This is done by bringing the gas into a glass globe of known capacity under definite conditions of temperature and pressure, and weighing this with the highest accuracy, using a similar flask as counterpoise.

DETERMINATION OF THE SPECIFIC GRAVITY OF A GAS

The specific gravity is usually determined by: (1) direct weighing, (2) the effusion method, or (3) the determination of the buoyant effect of the gas and air upon a body suspended in them.

By Direct Weighing.—The Lux Balance[1] which operates on the simple principle of weighing equal volumes of air and gas, the specific gravity being shown by the position of a pointer on a scale, gives fairly accurate results, but is not very extensively used.

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[1] *J. Gasbel.*, **35**, 251 (1887).

By Effusion Method.—This method is based upon the fact discovered by Graham [2] that the speeds of effusion of different gases are inversely proportional to the square roots of their densities. According to the kinetic theory of gases, the speed with which a gas will escape through a small opening in a thin plate must be proportional to the average speed of the molecules. Since the molecular speed is inversely proportional to the square root of the density, the rate of effusion must also be inversely proportional to the square root of the density. Therefore the times required for the escape of two gases through the small opening under the same pressure are directly proportional to the square roots of the densities of the gases, or the densities are directly proportional to the squares of their times of escape.

If a gas of the specific gravity s has a time of flow t, and another gas of a specific gravity s_1 has a time of flow t_1, the relation between the time of escape and the specific gravity is given by the equation

$$\frac{s_1}{s} = \frac{t_1^2}{t^2}.$$

If the specific gravity s of one of the gases be regarded as 1, the specific gravity of the other gas is found by the formula

$$s_1 = \frac{t_1^2}{t^2}.$$

This method was first used by Bunsen.[3] It was later modified by Schilling [4] for the examination of illuminating gas where large amounts of the gas are usually available. *A* (Fig. 33) is a glass tube of 40 mm. internal diameter and about 250 mm. long. The upper end is luted into a brass cover *C* into which is inserted the tube *B* through which the gas is led in. The gas escapes through a perforated platinum disk in the upper end of the tube *D*. A thermometer *T* is immersed in the water of the cylinder *K*. The inner cylinder has two marks, *M* and *N*. The apparatus is filled with water.

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[2] *Phil. Mag.*, (3) **2**, 175 (1833).

[3] Bunsen, *Gasometrische Methoden*, 2d ed., p. 184.

[4] Schilling, *Handb. d. Steinkohlengasbeleuchtung*, 3d. ed., p. 100.

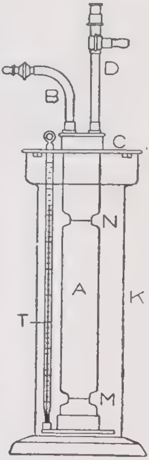

FIG. 33

To determine the specific gravity of an illuminating gas with this apparatus, the tube is first filled with air, and the time of escape of the air, under the prevailing temperature and pressure, is noted. The last trace of air is then removed by repeatedly drawing in and driving out the gas to be examined, and the time of escape of the illuminating gas is then observed. The squares of the values are directly proportional to the specific gravities of the gases. Since the specific gravity of air is usually taken as 1, the calculation is very simple.

The Schilling apparatus is open to objection because of the inconvenience in filling the inner cylinder with the gas under examination. Moreover, the marks are so far apart as to render the reading of them somewhat awkward. These drawbacks are avoided in the modification of the apparatus devised by Pannertz,[5] who uses two glass bulbs that are connected by a piece of rubber tubing.

Edwards[6] made a careful study of the theory and accuracy of this method for determining the specific gravity of a gas and he found that, although it is sufficiently accurate for control work where only relative values are needed, it does not give results of high accuracy, errors being at times as high as 10 per cent. He recommends a modification of the apparatus as shown in Fig. 34, with either mercury or water as the confining liquid. If the apparatus is to be used with water only, the bulb *A* may be omitted. If calibrated orifices are used and precautions are taken to prevent the condensation

[5] *J. Gasbel.*, **48**, 901 (1905).

[6] *Bureau of Standards, Tech. Paper* No. 94; *Met. Chem. Eng.*, **16**, 518 (1917); Buckingham and Edwards, *Bureau of Standards, Sci. Paper* No. 359.

of water in the orifice, it is possible to secure results accurate to about two per cent.

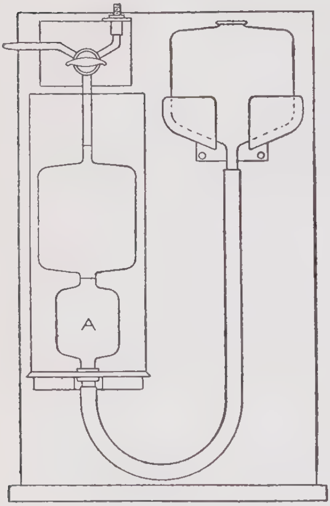

FIG. 34

If water is used as the confining liquid, the result will be quite different from that which is obtained when mercury is employed and the gas is dry (see p. 32) but one value can readily be calculated from the other by the following equations,

$$S_s = \frac{(S + k)}{(1 + k)}$$

and

$$S = S_s(1 + k) - k$$

where S = specific gravity, S_s = specific gravity of saturated gas referred to saturated air, and k is a value depending upon the density and partial pressure of the water vapor. In most cases the effect of change of pressure is negligible.

TABLE IV

VALUES OF k AT 760 MM. AND VARIOUS TEMPERATURES [7]

TEMPERATURE 0° C.	k
0	0.004
5	0.005
10	.008
15	.011
20	.015
25	.020
30	.027

Other forms of effusion apparatus have been suggested by Myhill,[8] Hofsäss,[9] Wilson,[10] and Wailes.[11]

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[7] Edwards, *loc. cit.*

[8] *Gas World*, **58**, 763 (1913).

[9] *J. Gasbel.*, **56**, 841 (1913).

[10] *Gas Age-Record*, **50**, 321 (1922).

[11] *Gas Age-Record*, **51**, 732 (1923).

By Buoyant Effect.—This method is based upon the laws of compressibility and the buoyancy of gases. According to Boyle's law the density of a gas is proportional to its pressure, and the buoyant effect of the gas upon a body suspended in it is proportional to its density, and therefore is proportional to its pressure. If then the buoyant effect upon a body is made the same when suspended in two different gases, the densities of the gases must be the same at those presures, or the densities at normal pressures are inversely proportional to the pressures on the two gases when they exert an equal buoyant force.

This method was first used by Gray and later by Aston,[12] Gray, Ramsay and Baxter. Edwards [13] has designed a portable apparatus (Fig. 35) working on this principle, which is capable of giving results accurate to one part in a thousand.

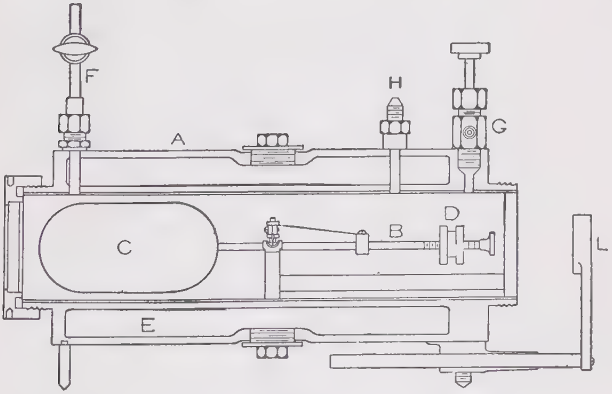

FIG. 35

The balance consists of a beam *B* carrying a sealed globe *C* on one end, and a counterweight *D* on the other. The balance beam with its support is mounted in a gas-tight chamber *A* made of brass or aluminum surrounded by a water jacket *E*.

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[12] *Proc. Roy. Soc.*, London [A] **89**, 439 (1914).

[13] *Bureau of Standards, Tech. Paper* No. 89 (1917); *Ind. Eng. Chem.*, **9**, 790 (1917).

The ends of the chamber *A* are closed by brass screw-caps with glass windows. An adjustable lens *L* through which the cross-hairs in the window and on the end of the beam are observed, enables the operator to determine when the beam is balanced (brought back to the original mark). The chamber *A* has three openings, *F* for filling the chamber with dry air or dry gas, *G* a needle valve for removing the excess of the gas, and *H* for connecting the chamber to a mercury manometer. The chamber is also equipped with levelling screws and should be provided with two spirit-levels at right angles to each other.

To determine the specific gravity of a gas, the chamber *A* is filled through the inlet *F* with dry air free from carbon dioxide and dust, and the pressure is adjusted by removing the excess air through the needle valve *G* until the beam is balanced. The pressure on the mercury manometer and the barometric pressure are read. The chamber *A* is then evacuated through *G* and is filled with the dry gas. The pressure is again adjusted until the beam balances, and the manometer and barometer are again read. The specific gravity of the gas is then calculated as follows, taking the density of dry air free from carbon dioxide as unity.

$$S = \frac{P_a}{P_g} \qquad \text{where}$$

$S =$ specific gravity of the gas,
$P_a =$ pressure (manometer pressure plus atmospheric pressure) when the beam balances in air.
$P_g =$ pressure (manometer pressure plus atmospheric pressure) when the beam balances in the gas.

If desired, a gas other than air may be used as a standard of comparison.

The possible sources of error in this method are: (1) deviations of the gases from Boyle's law, (2) compressibility of the globe, (3) condensation upon the beam, (4) solid particles adhering to the beam, (5) errors in reading of pressure, and (6) incomplete replacement of the gas in the apparatus. However, with careful manipulation excellent results may be obtained with this balance.

Baxter[14] has applied this same principle in determining the density of air, and Stock and Ritter[15] have described two forms of micro-gas-balances similar to that of Edwards.

Devices for the determination of specific gravity by the measurement of the differential pressure at an orifice,[16] and also by the measurement by displacement interferometry[17] have been described.

[14] *J. Am. Chem. Soc.*, **43**, 1317 (1921).

[15] *Z. physik. Chem.*, **119**, 333 (1926).

[16] *Chem. Ztg.*, **38**, 20 (1914); Weymouth, Anderson and Fay, *Ind. Eng. Chem.*, **15**, 358 (1923).

[17] Barus, *Proc. Nat. Acad. Sci.*, **10**, 153 (1924).

CHAPTER V

ARRANGEMENT AND FITTINGS OF THE LABORATORY

The room for gas analysis should have a northern exposure and large windows, and the temperature should be uniform. The lighting should be sufficient to enable the operator to make his readings without being obliged to turn toward the windows. The floor should be free from cracks, and should slope slightly toward the middle in order that any spilled mercury may easily be brought together and taken up. A cement floor covered with some form of mastic is very satisfactory. If the floor is of wood, it should be covered with linoleum. Mercury should not be allowed to lie on the floor because it may lead to poisoning [1] of the operators. The room should further be provided with gas, running water, and a large sink, the sink being fitted with an iron "S" trap, the lower bend of which is bored, threaded, and provided with a screw plug to permit the easy removal of any mercury that may collect in the trap.

An ample supply of water of the temperature of the room may cheaply be provided by placing, near the ceiling and above the sink, a cylindrical galvanized iron tank of about 400 liters capacity and fitted with a gauge glass. The tank is filled through a small iron pipe connected directly to the water supply. An overflow pipe in the top of the tank reaches down into the sink. A tank of this size provides an adequate supply of water both for analytical work and for use in a gas calorimeter.

The laboratory should also contain a barometer, accurate thermometers, air under pressure, and water suction-pumps at the working tables. Both direct and alternating electric current are also necessary, the former being supplied either by storage batteries or from a direct-current generator. A small induction coil is needed for the analysis of gas mixtures by explosion, and rheostats should be fastened to the wall near the electric current supply for the analysis by combustion. It is also desirable to house the calorimeter in a cabinet near the large water-tank.

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[1] Stock, *Z. angew. Chem.*, **39**, 461 (1926); Dennis, *Ind. Eng. Chem.*, **18**, 205 (1926).

When the laboratory is used for student instruction, it is convenient to have adjacent to it a room for the storage of apparatus. This room should also provide space for mercury purifiers and stills, and if coal analyses are to be made, a heavy shelf should be fastened to the wall for use in filling calorimeter bombs.

In the Cornell laboratory for gas analysis, the adjacent storeroom has a large hood in which stand gasometers of 130 liters capacity. Gas mixtures for student analyses are prepared and stored over water in these gasometers, and a series of pipes carries the various mixtures to each working place in the laboratory.

CHAPTER VI

APPARATUS FOR GAS ANALYSIS WITH WATER AS THE CONFINING LIQUID

THE HEMPEL SIMPLE GAS BURETTE (FIG. 36)[1]

This consists of two glass tubes *A* and *B* which are set in iron feet *F* and *D*, and are connected by a rubber tube of 7 mm. internal diameter, 12 mm. external diameter, and about 120 cm. long. To facilitate the cleaning of the burette the rubber tube may be divided in the middle and the two ends joined by a piece of glass tubing. The tubes *A* and *B* are bent at right angles inside the feet, and the projecting ends are about 4 mm. external diameter and are somewhat corrugated so that the rubber tubes may be tightly fastened to them by wire ligatures.

The measuring tube *A* ends at the top in a capillary tube *C* of 1 mm. internal diameter, 6 mm. external diameter,[2] and about 3 cm. long. Over this a short piece of soft rubber tubing, 3 mm. internal diameter, and 6.5 mm. external diameter, is wired[3] on. The rubber tube is closed by a Mohr pinchcock *E* which is put on close to the end of the capillary. A burette terminating in a glass stopcock has been recommended by some,[4] but this renders the apparatus fragile and costly, and has no compensating advantage in this apparatus for technical analysis. A stopcock at the top of the burette also prevents the easy jacketing of the tube (see below). If the apparatus is properly manipulated during the analysis, the rubber tube does not come in contact with more than traces of the absorbent and will remain in good condition for a considerable length of time. It should, however, be tested from time to time to make sure that it does not leak. The pinchcock should always be taken off from the rubber tube after use, as this helps to keep the latter in good condition. Notwithstanding the fact that readings cannot be made under the rubber tube, no measurable error results therefrom because of the small internal diameter of the capillary tube *C*, the variations in the readings being less than a tenth of a cubic centimeter. The graduated measuring tube *A* contains 100 cc., the lowest mark being slightly above the iron foot. The cubic centimeters are divided into fifths, and the numbers run both up and down. The level-tube *B* is somewhat widened at the upper end to facilitate the pouring in of the confining liquid.

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[1] The Hempel apparatus for technical gas analysis is constructed according to the Cornell specifications by Greiner and Friedrichs, Stützerbach in Thüringen, Germany.

[2] All capillary tubing of the Hempel burettes and pipettes should have these dimensions.

[3] Keane and Patchin, *J. Soc. Chem. Ind.*, **38**, 391 (1919), have advocated a small metal clip for this purpose with burettes having a glass stopcock.

[4] White and Campbell, *J. Am. Chem. Soc.*, **27**, 734 (1905); Moldenhauer, *Z. angew. Chem.*, **37**, 424 (1924).

It should be borne in mind that with the Hempel apparatus for technical gas analysis, as with any other form of apparatus, errors so large that they may entirely destroy the value of the analysis will result when the reagents and the confining water do not have the temperature of the laboratory, or when there is appreciable change in temperature during the brief time necessary for the analysis. A rise of temperature of only one degree would cause an error of 0.3 per cent in a total volume of 100 cc., which makes it evident that the analysis should be made in a laboratory that is of nearly constant temperature.

If the work must be done outside of the laboratory under fluctuating temperature, the burette should be surrounded with a water jacket. The jacketing of the Hempel burette may easily be effected by slipping down over the burette an inverted single-bore rubber stopper about 4 cm. in diameter, and slipping over the burette and upon the stopper a large glass tube somewhat shorter than the burette, holding the upper end in place by means of a split cork. The larger tube is then filled with water.

GAS PIPETTES

In the Hempel method of gas analysis, the absorbable constituents of a gas mixture are successively removed by passing the gas into a series of gas pipettes containing suitable reagents. The construction of these pipettes is such as to render it possible to bring the gases into intimate contact with the absorbents. The pipette may even be disconnected from the burette and vigorously shaken. There must be at least as many pipettes as there are absorbable constituents in the gas mixture.

The gas pipettes are made in several different forms, the type that is used depending upon the character of the reagent and the technique of the absorption.

THE HEMPEL SIMPLE ABSORPTION PIPETTES

These are modifications of the Ettling gas pipette, first used by Doyere for the absorption of gases, and they are filled with such absorbing liquids as are not affected by the air.

The Hempel Simple Absorption Pipette for Liquid Reagents

As originally designed this consisted of two large bulbs *H* and *I* (Fig. 36) joined by the tube *J*, and a capillary tube *K* of 1 mm. internal diameter, and 6 mm. external diameter, bent as shown in the figure. This form is used when it is desired to inclose the gas in the pipette between two columns of liquid, in which case the distance *M* must be greater than *N*. White and Campbell[5] have advocated a modification of the gas pipette in which the tube *K* extends vertically from *I*, but Anderson[6] found this to be undesirable and he gave to the capillary tube *K* the shape shown in Fig. 38 and introduced a small enlargement, 3 mm. internal diameter, in the tube to prevent drops of the reagent from passing over into the burette. This form has been found to be very satisfactory for analyses with this apparatus.

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[5] *J. Am. Chem. Soc.*, **27**, 734 (1905).

[6] *J. Ind. Eng. Chem.*, **6**, 237 (1914).

The bulb *H* (Fig. 36) holds about 100 cc., and *I* about 150 cc., so that when 100 cc. of gas is brought into *I*, sufficient space for the absorbing liquid will remain. To protect the pipette from being broken and to facilitate its manipulation, it is fastened to a wooden or iron stand.

An iron stand is preferable to wood because its greater weight renders it more stable and because it cannot warp out of shape. An iron stand with a four-sided base is superior to one with legs only at the ends because with the latter form of base there is danger that one leg of the pipette may be pushed over the edge of the stand (see Fig. 36) and the apparatus fall and be broken.

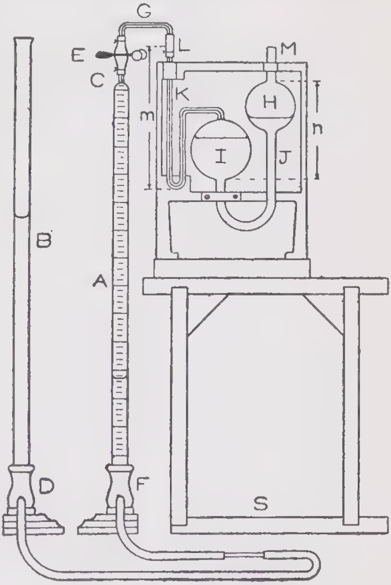

Fig. 36

The pipette is fastened in the iron standard at the three points shown in Fig. 36. The capillary tube and the tube above *H* are slipped through openings in the upper bar of the frame and the tube below *I* is set back against the lower crossbar. This small plate that closes this lower opening is then fastened in place by screws, and the spaces between the three tubes and their iron collars are filled with Plaster of Paris. It is well to bring the Plaster of Paris up around the lower part of *I* for the purpose of giving the bulb additional support. If the pipette is broken, the plate is unscrewed, the glass parts and the Plaster of Paris are broken out and a new pipette is slipped into place and fastened as above described. With the style of mounting here recommended, the breakage of the Hempel pipettes is very slight, and the life of the apparatus is much greater than when the pipettes are mounted on light wooden frames, or are held in place by clamps and corks as some writers have advised.

The capillary tube should project from two to three cm. above the frame. A short piece of rubber tubing is wired on the free end of the capillary.

A special form of this pipette for use with fuming sulphuric acid and with nickel cyanide is shown in Fig. 37. The small upper absorption bulb *B*, about 5 cm. in diameter, is filled by the glass-blower with pieces of broken glass or glass beads which serve to increase the surface of contact between the gas and the reagent. When broken glass or glass beads are used in gas pipettes there is danger that some gas may be trapped between the pieces of glass. This may usually be avoided by drawing the liquid very slowly into the bulb that contains the broken glass. Another form [7] has been recommended by Friedrichs to overcome this difficulty but it does not give as good contact between the gas and the reagent. The liquid is introduced into the pipette through *A*. When the pipette is not in use *A* and *C* are covered with small glass caps made from glass tubing.

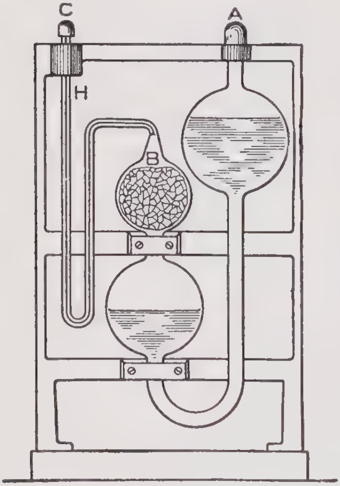

Fig. 37

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[7] *Z. angew. Chem.*, **29**, 1, 207 (1916).

The Hempel Simple Absorption Pipette for Solid and Liquid Reagents

The only difference between this and the simple pipette is that in place of the bulb *I* (Fig. 36) there is inserted the cylindrical part *A* (Fig. 38), which can be filled with solid substances through the neck *N*. This neck is closed by a cork or rubber stopper which is held in place by a wire.

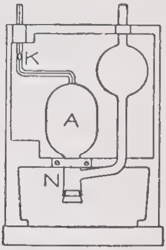

FIG. 38

A glass tube closed at the top, and over which a rubber ring, cut from a rubber tube, is drawn, also makes a good stopper. By this arrangement only a narrow strip of rubber is exposed to the action of the reagent.

Pipettes of this form are used for the determination of carbon dioxide by sodium hydroxide, and of oxygen by means of phosphorus (see p. 181). In the latter case it is necessary to protect the reagent from the action of the light when the pipette is not in use, which is done either by covering the pipette with a light box, or by making the cylinder *A* of brown glass.[8]

THE HEMPEL DOUBLE ABSORPTION PIPETTES

Reagents that are acted upon by oxygen, such as alkaline pyrogallol, cuprous chloride, and ferrous salts, cannot, of course, be kept in the above forms of pipette because the reagent would become inactive in a short time through contact with the air. Hempel first sought to avoid this difficulty by protecting the reagent with a layer of high-boiling petroleum, after first convincing himself that the tension of the petroleum, resulting from its solubility in the reagent, did not cause a perceptible error. It was soon found, however, that although such hydrocarbons decidedly lessen the access of air, they do not by any means form a perfect protection. Further experiment on this subject led to the construction of

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[8] Friedrichs, *J. Am. Chem. Soc.*, **34**, 1513 (1912); *Z. angew. Chem.*, **25**, 1905 (1912).

The Hempel Double Absorption Pipette for Liquid Reagents (Fig. 39)

This pipette permits the use of the reagents in question under an easily movable atmosphere that is free from oxygen, and the reagent may be kept saturated with those constituents of the gas that it does not strongly absorb, which is a great advantage. The pipette consists of the large glass bulb *A*, of about 150 cc. capacity, and three smaller bulbs, *B*, *C* and *D*, each containing only 100 cc. They are connected by the bent tubes *E*, *F* and *G*, and end in the bent capillary tube *K*.

The pipette is fastened to an iron stand in the manner already described (see p. 61).

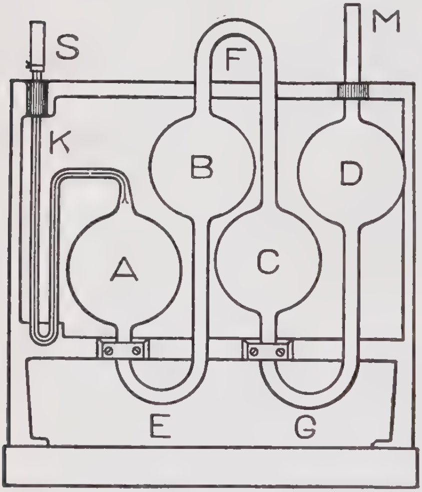

Fig. 39

The pipette is prepared for use by slipping into the rubber tubing at *S* a capillary tube which is so bent as to extend down into a bottle containing the solution of the absorbent. By attaching a water suction-pump at *M*, the liquid is drawn into the bulbs *A* and *B* through the capillary *K* until bulb *B* is partially filled. The suction pump is then disconnected, and air is blown by the mouth through a rubber tube attached to *M*, forcing the air in *A* out through the capillary *K*. If the operation has been performed properly the absorbing liquid will fill the capillary *K*, the bulb *A*, and the connecting tube *E* up to bulb *B*, and *B* will be empty. The tube extending into the bottle containing the absorbing solution is now disconnected at *S* and suction is applied at *M* until the absorbent is drawn up to the top of bulb *B*, if the reagent does not absorb oxygen. *S* is then closed with a pinchcock, and water is poured into *M* until the bulb *D* is full. Upon opening *S* and gently blowing into *M*, water will rise in *C* and the reagent in *A*, and if the filling has been properly performed the reagent will stand at the top of the capillary *K* when the water in the bulb *C* reaches the top of that bulb.

If the reagent absorbs oxygen, then after *A* has been filled with the solution, the liquid should be drawn up in *B* only to about two-thirds of the height of *B* before the introduction of the water. The bulb *D* is next filled with water in the manner already described. Upon the absorption of the oxygen from the air in the bulb *C* by the reagent, there will remain between the liquids in the bulbs *B* and *C* the desired volume of gas, about 100 cc.

Several writers have suggested[9] that there be an opening at the top of tube *F* for convenience in filling and cleaning the pipette.

A double form of this pipette having duplicate bulbs *A* and *B*, joined together at *F* and connected by a stopcock at *K*, has been designed by the United Gas Improvement Company for use with cuprous chloride.

The Hempel Double Absorption Pipette for Solid and Liquid Reagents (Fig. 40)

The construction may easily be understood from the figure. To prepare this double pipette for use, turn it upside down, introduce through the neck *N* of the bulb *A* the solid substance to be employed, close the neck with the stopper, and wire the stopper in place. Bring the pipette into an upright position and fill it with liquid in the manner described above. An excellent modification of this pipette for use with an alkaline solution of pyrogallol has been designed by Anderson,[10] and is shown in Fig. 41.

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[9] Fleissner, *Chem. Ztg.*, **32**, 770 (1908); Göckel, *Z. angew. Chem.*, **26**, 1, 616 (1913); Cumming, *J. Soc. Chem. Ind.*, **32**, 9 (1913); Hefter, *Chem. Ztg.*, **48**, 142 (1924).

It differs from the usual pipette in that the bulb for the reagent is replaced by a cylinder which is cone-shape at its top. The cylindrical portion of the usual double pipette is much larger than is necessary when thin-walled glass tubes are used to increase contact, and it is desirable to have as small a bulb as possible in order to decrease the volume of the space between the upper ends of the tubes and the top of the bulb.

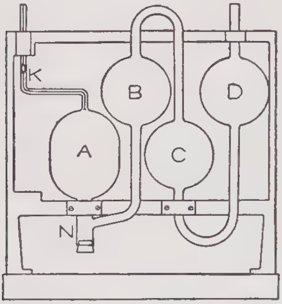

FIG. 40

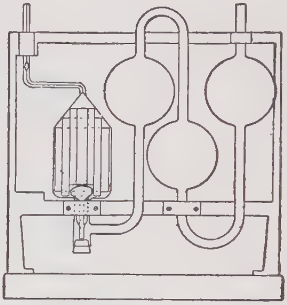

FIG. 41

While the reagent in the simple pipette may be considered to be saturated with gas only when it is kept in continual use, that in the double pipette, on the contrary, remains saturated for an exceptionally long time, since diffusion must take place through the confining 100 cc. of water and through the narrow tube that connects the bulbs *C* and *D* (Fig. 39).

MANIPULATION OF THE HEMPEL APPARATUS

If the burette has been in use, clean it thoroughly, and rinse it well with water. Examine the rubber tubing attached to the capillary of the burette to see that it is intact and that the wire ligature is in good condition. Make sure that the pinchcock closes the rubber tubing completely. Open the pinchcock *E* (Fig. 36) and slip it down over the capillary tube. Into the open end of *B* pour water that has been saturated with the gas mixture that is to be analyzed until *A* and *B* are rather more than half full.

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[10] *J. Ind. Eng. Chem.*, **8**, 133 (1916).

Filling Burette with Confining Liquid.—Drive out all air from the large rubber tubing connecting *A* and *B* by raising and lowering the tubes alternately, keeping the rubber tubing taut during this operation. Grasp the iron base *D* in the left hand and raise it until the water begins to flow out of the top of the burette. Then close the rubber tube of the burette with the pinchcock, setting the pinchcock up close to the end of the capillary. Compress the rubber tubing at *D* between the thumb and fingers of the left hand and pour out the excess of water that is in *B*.

Measurement of 100 cc.—To measure off exactly 100 cc. of the gas sample, insert into the rubber tube at the top of the burette a capillary tube connected with the gasometer or pipe from which the sample is to be taken, after first displacing the air in this connecting capillary by the gas to be examined. Grasp the upper part of the level-tube *B* (Fig. 36) in the left hand. Lower it below *A* and open the pinchcock *E* with the right hand. Draw somewhat more than 100 cc. of gas into the burette. Close the pinchcock *E*, place the level-tube on the table and allow the water in the burette to run down for one minute.[11] Disconnect the capillary tube from the gasometer, raise the level-tube with the right hand until the gas in the burette is compressed to a volume less than 100 cc. and then close the rubber tubing at *G* tightly by squeezing it close up to the lower end of the burette between the thumb and first finger of the left hand. Place the level-tube on the table, grasp the iron base of the burette with the right hand and keeping the rubber tubing at *G* still tightly compressed raise the burette until the meniscus of the water in it is on a level with the eye. Then gradually release the pressure on the rubber tubing until the water in the burette falls exactly to the 100 cc. mark. Compress the rubber tube again, place the burette on the table and open the stopcock *E* for a moment to permit the excess of gas to escape. The burette should now contain 100 cc. of the gas under atmospheric pressure. To ascertain whether this is the case, grasp the base of the burette in the right hand and of the level-tube in the left hand and holding the burette perpendicularly lay the level-tube at an angle across it, and bring the water in the two tubes to the same level. If the measurement of the sample has properly been made, the water in the burette will stand exactly at the 100 cc. mark.

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[11] See p. 93.

Absorption of a Gas.—To remove an absorbable constituent of the gas, the burette and proper absorption pipette are connected in the manner shown in Fig. 36. Place the burette and level-tube on the table, the level-tube *B* at the left, bring up near the side of the burette the wooden stand *S*, and place on the stand a pipette containing the proper absorbent.[12] Insert in *L* the bent glass capillary tube *G*. These connecting capillary tubes are of the same dimensions as the capillary tubes of the burette and pipette, namely, 6 mm. external diameter and one mm. bore. The horizontal portion is about 6 cm. long and the legs each about 2.5 cm. long. Slip a piece of rubber tubing about 30 cm. long over the tube *M* of the pipette. Grasp *G* between the thumb and fingers of the right hand, squeeze the rubber tube *E* on the capillary of the burette between the thumb and fingers of the left hand, blow gently through *M* until the liquid in the pipette is driven to the farther end of the connecting capillary tube *G* and then insert the end of *G* into the rubber tube on the burette. If the connection is properly made there will be practically no movement of the reagent in the connecting capillary tube.

Even if a linear centimeter of air should appear in the capillary, the error arising therefrom may be disregarded, since capillary tubing with a bore of about one mm. contains only about 0.01 cc. in one linear cm. If, however, after *G* has been inserted in *E*, more than a linear centimeter of air appears in *G*, it shows that the connection was carelessly made, and *G* should be slipped out of *E* and the operation repeated.

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[12] Krone, *J. Ind. Eng. Chem.*, **8**, 231 (1916), has described a special stand for holding the Hempel apparatus.

Certain reagents should never be allowed to come into contact with the rubber tube at *L*. In such case the liquid is forced upward in the capillary of the pipette until it stands just below the iron of the frame. If quite accurate results are desired, allowance should be made for the very small amount of air thus left in the connecting capillary tubes. This may easily be done by measuring the length of the capillary tube that is empty of liquid. Every ten centimeters of length corresponds to 0.1 cc. of air. This correction is not necessary in ordinary technical analysis.

When the pipette and burette have been connected in the manner above described the pinchcock on *E* is opened, the level-tube *B* is slowly raised and the gas is driven over into the pipette. Water is allowed to flow into the capillary *G* until it reaches the point in the bend of that tube to which the reagent had been driven over. The pinchcock at *E* is then closed. This manipulation leaves the capillary tube of the pipette and the greater part of the bent connecting capillary tube filled with the gas mixture under examination together with such portion of the reagent as adheres to the walls of these capillary tubes. This adhering reagent suffices to remove the greater part of the absorbable constituent in the gas mixture because a slender column of the gas stands in contact with a comparatively large surface of the reagent, but even if the absorbable constituent should constitute 40 per cent of the gas mixture, and only half of this gas in the capillary tubes should be absorbed by the reagent on the walls, the error thus caused would be negligible in technical analysis. This is apparent when we consider that the total length of the two capillary tubes is about 40 cm. and that the volume of gas in these tubes is, consequently, about 0.4 cc. The volume of the absorbable constituent would then amount to 0.16

cc. and if only half of this were absorbed the error would be 0.08 cc. These figures illustrate an extreme case. If the absorbable constituent amounted to not more than 20 per cent of the gas mixture and if, as may usually be expected, 80 per cent of it were absorbed, the error due to incomplete removal of this constituent in the capillary tubes would be less than 0.02 cc. After the constituent that is to be removed has been entirely absorbed, the gas is drawn back into the burette. This is done by grasping the level-tube with the left hand and bringing it into such position that the confining liquid in it stands slightly lower than that in the burette. The pinchcock *E* is opened, the level-tube is slowly lowered and the gas is drawn back into the burette until the liquid from the pipette reaches the same point in *G* at which it originally stood. The pinchcock *E* is now closed, the water in the burette is allowed to run down for one minute, and the gas volume in the burette is then read in the manner above described.

It frequently happens that complete absorption of the gas can be accomplished only by shaking the pipette after the gas has been driven over into it. In such case a second pinchcock is placed on the rubber tube *L*, and after the gas has been transferred to the pipette, both *E* and *L* are closed. The frame of the pipette is now grasped in the right hand, the burette is steadied with the left hand, and the absorbent is brought into intimate contact with the gas by gently rocking the stand backward and forward on the front edge of its base.

If the reagent has no appreciable effect upon rubber, much time may be saved in making the connection between pipette and burette by preparing the pipette in such manner that it will stand ready at all times for connection with the gas burette. This is done by placing a pinchcock upon the rubber tube of the pipette, inserting into this tube the bent connecting capillary tube, and then, holding the pinchcock open, driving the reagent over nearly to the further bend of this connecting capillary by blowing into the large rubber tube attached to

M. The pinchcock is then closed. If the operation has been correctly performed, the reagent should now stand close to the bend in the connecting capillary tube that is nearest the burette. The capillary tube is next inserted in the rubber tube of the burette and the absorption is made in the manner above described. After the absorption of the gas, the reagent is drawn over nearly to the further bend of the connecting capillary tube, and the pinchcock on the pipette is then closed. This should drive the reagent to about the same point in the connecting capillary as that at which it first stood. The capillary tube is now withdrawn from the rubber tube that is attached to the top of the burette, and the pipette is removed. The pipette, with the bent capillary tube attached to it, now stands filled with the reagent to the further bend of the connecting capillary and is ready for immediate connection with the burette when another determination of the same constituent gas is to be made.

The manipulation of the pipette filled with solid absorbents is still simpler, for in this case no shaking is necessary because of the large surface of contact between the solid and the gas.

The Hempel apparatus for technical gas analysis possesses many points of superiority over other forms of apparatus. It is not fragile and if a part is broken it is easily replaced. It contains no stopcocks. It is easily cleaned. Either water or mercury may be used as the confining liquid. When water is employed, it is easily saturated with the gas mixture under analysis. The pipettes avoid waste of reagent and protect the reagents from the air. The removal of absorbable constituents of a gas mixture may rapidly and completely be effected.

It must be conceded that the Hempel apparatus is not easy to carry about, but for the analysis of rather simple gas mixtures Dennis[18] has obviated this objection by the design of a portable Hempel apparatus.

Accuracy of Analyses with the Hempel Apparatus.—The criticism has been urged against the Hempel apparatus that

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[13] Dennis, *Gas Analysis* (1913), p. 69.

it is cumbersome, and that as a consequence rapid analytical work cannot be performed with it. Those who are familiar with the manipulation of the various standard forms of apparatus for technical gas analysis will, however, probably concur in the statement that an analysis of any of the usual gas mixtures can be performed with the Hempel apparatus with as great or even greater speed than that attainable with almost any other device, and with an accuracy that far surpasses that of most other technical methods, and approximates that obtained over mercury. This is shown by two partial analyses of illuminating gas:

TABLE V

I. Technical Analysis	II. Technical Analysis	Exact Analysis over Mercury
1.6 per cent	1.5 per cent	1.5 per cent carbon dioxide
3.1 " "	2.9 " "	3.0 " " heavy hydrocarbons
1.4 " "	1.6 " "	1.4 " " oxygen

OTHER FORMS OF APPARATUS

Pfeiffer[14] has advocated a form of the Hempel apparatus with a special stopcock to eliminate the errors due to capillary space, but this modification can scarcely be regarded as an improvement.

A modification of the Hempel burette known as the modified Winkler gas burette[15] is of use in the determination, directly in the burette, of gases that are readily soluble in water, such as ammonia or hydrogen chloride, since the initial volume of gas can be measured without bringing it into contact with water. However, when a gas mixture contains gases that are easily soluble in water, it is generally preferable to pass a large volume of the gas mixture through a suitable absorbent, and to then determine the absorbed gas by titration. King[16] has described an apparatus for testing a gas mixture for acid and alkaline constituents by means of the color change of a suitable indicator.

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[14] *J. Gasbel.*, **42**, 209 (1899).
[15] Dennis, *Gas Analysis* (1913), p. 70.
[16] *J. Soc. Chem. Ind.*, **38**, 33 T (1919).

The Honigmann[17] gas burette is suited only to the rapid and approximate determination of fairly high percentages of carbon dioxide.

The Bunte[18] gas burette, which is a development of a simpler form of apparatus of Raoult,[19] may be used for the approximate determination of carbon dioxide and oxygen. Determinations with this burette cannot be accurate, since the gas in the burette is brought into contact with large volumes of water that are unsaturated with the gas mixture, and which will therefore absorb some of the gas of the sample.[20] The Bunte burette has been used in combination with absorption pipettes in many forms of apparatus such as that of Jaeger.[21] This form of burette is also wasteful of reagent, since the reagent which has once been employed cannot be used over again because of dilution. The same objection may also be raised against the apparatus of Elliott[22] and others.[23]

THE ORSAT APPARATUS

In the analysis of commercial grades of sodium carbonate there early arose a demand for a rapid and convenient method for the determination of carbon dioxide, which was met in 1868 by the apparatus designed by Schlösing and Rolland.[24] In 1874 Orsat patented a device[25] which was based directly upon the principle of the apparatus of those authors, and which attracted considerable attention at the time and rapidly came into general use. Because of its compactness and ease of manipulation, the Orsat apparatus has been and still is very generally employed by gas analysts. In its original form, however, and even in some of the later modifications it possesses certain inherent faults, and the unsatisfactory character of the analytical results that are obtainable with it is evidenced by the many changes in its construction that have been proposed by Fischer,[26] Lunge,[27] Hankus,[28] Sodeau,[29] Meyer,[30] Nowicki,[31] Heinz,[32] Hahn,[33] United States Steel Corporation,[34] Williams,[35] Dennis,[36] Lomschakov,[37] Wempe,[38] Anderson,[39] United States Bureau of Mines,[40] Bürgerhausen,[41] Aschof,[42] and Mezger and Müller.[43] The chief objection to the apparatus is the incompleteness of the absorption of such gases as oxygen and carbon monoxide. The researches of Gautier and Clausmann, Bendemann, Hankus, Hempel, Norwicki, Hahn, Dennis and Edgar, and others have demonstrated that the complete removal of oxygen by alkaline pyrogallol and of carbon monoxide by cuprous chloride can be effected only when the absorbent and the gas are shaken together, or when the gas is, in some manner, brought into prolonged and intimate contact with the absorbent. Many of the modifications that have been suggested have had to do with change of form of the absorption pipette with the object of increasing the rapidity or the completeness of the removal of the absorbable constituent. This has been done either by giving the pipette a form in which absorption is accelerated by increasing the surface of the reagent that is in contact with the gas, *e.g.*, the Orsat and Anderson pipettes, or by a form in which the same result is obtained by passing the gas through the reagent in such a fashion as to secure very intimate contact, as in the Hankus, Nowicki-Heinz, or Dennis pipette. With most of the suggested forms of the Orsat absorption pipette, the removal of oxygen and carbon monoxide is quite incomplete unless the gas is allowed to stand in contact with the absorbent for a very considerable length of time, or is passed back and forth many times between the burette and pipette. Failure to recognize this inadequacy of the apparatus frequently results in the incomplete removal of oxygen, and, as a consequence, a decrease in volume is observed when the gas mixture is next passed into the cuprous chloride pipette. In very many cases the analyst has in this manner been led into reporting carbon monoxide in a gas mixture, such as flue gas, when in fact no carbon monoxide is present, the decrease in volume being due solely to the absorption, by cuprous chloride, of oxygen that still remains in the gas mixture.

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[17] Dennis, *Gas Analysis* (1913), p. 72.

[18] *Dingl. polyt. J.*, **228**, 529 (1878); Dennis, *Gas Analysis* (1913), p. 74.

[19] *Compt. rend.*, **82**, 844 (1878).

[20] Haber, *J. Gasbel.*, **39**, 802 (1926), has suggested a method of manipulation to lessen the error.

[21] *J. Gasbel.*, **41**, 264 (1898); *Z. angew. Chem.*, **12**, 173 (1899).

[22] *J. Soc. Chem. Ind.*, **29**, 192 (1910).

[23] Lowe, *J. Soc. Chem. Ind.*, **41**, 11 T (1922); Jones, *ibid.*, **44**, 115 (1925); Murray, *J. Chem. Soc.*, **127**, 769 (1925).

[24] *Ann. Chim. Phys.*, **14** [4], 55 (1868).

[25] *Chem. News*, **29**, 177 (1874).

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[26] Fischer's *Jahresber.*, **26**, 330 (1880).

[27] *Dingl. polyt. J.*, **245**, 512 (1882).

[28] *Öesterr. Chem. Ztg.*, **47**, 81 (1889); *J. Gasbel.*, **49**, 367 (1906).

[29] *Chem. News*, **89**, 61 (1904).

[30] *Z. angew. Chem.*, **18**, 446 (1905).

[31] *Öesterr. Zeit. f. Berg. Hütt.*, **53**, 337 (1905).

[32] *J. Gasbel.*, **49**, 367 (1906).

[33] *Loc. cit.*

[34] *Met. Chem. Eng.*, **9**, 303 (1911).

[35] *Ind. Eng. Chem.*, **4**, 380 (1912); *Met. Chem. Eng.*, **10**, 382 (1912).

[36] *Ind. Eng. Chem.*, **4**, 898 (1912).

[37] *Chem. Ztg.*, **37**, 1262 (1913).

[38] *Z. angew. Chem.*, **27**, 271, 284 (1914).

[39] *Ind. Eng. Chem.*, **8**, 133 (1916).

[40] Burrell and Siebert, *Bulletin* 42 (1913); *Technical Paper* 14 (1913); Burrell and Oberfell, *Ind. Eng. Chem.*, **8**, 228 (1916); Suydam, *Ind. Eng. Chem.*, **9**, 972 (1917); Jones and Neumeister, *Met. Chem. Eng.*, **21**, 734 (1919); Fieldner, Jones and Holbrook, *Technical Paper* 320 (1925); Burrell, Siebert and Jones, *Bulletin* 197 (1926).

[41] *Chem. Ztg.*, **43**, 731 (1919).

[42] *Chem. Ztg.*, **45**, 582 (1921); *Stahl u. Eisen*, **41**, 1406 (1921).

[43] *Gas u. Wasserfach*, **64**, 633 (1921).

Several interesting and some valuable suggestions for increasing the completeness and rapidity of absorption in the Orsat apparatus have appeared in chemical journals, as for example the proposal [44] to use two pipettes for the absorption of oxygen by alkaline pyrogallol and two for the removal of carbon monoxide by cuprous chloride. This would undoubtedly lessen the errors of the determinations but would hardly remove them entirely. More worthy of consideration are the proposed modifications of the form of the absorption pipette to bring gas and liquid into intimate contact.

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[44] Bendemann, *J. Gasbel.*, **49**, 853 (1906).

An experimental study of some of the different forms of Orsat pipettes has been made[45] by comparative determinations of oxygen in atmospheric air by means of an alkaline solution of pyrogallol (see p. 174). This investigation showed that the complete absorption of oxygen from air can be accomplished with the Orsat, Hankus, and U. S. Steel Corporation forms of pipette only by repeated passage of the gas sample into the pipette and back into the burette. The Nowicki-Heinz and Dennis forms of pipette were of nearly equal efficiency, but the former is open to the objections that the gas is frequently trapped in the spiral and it is very fragile.

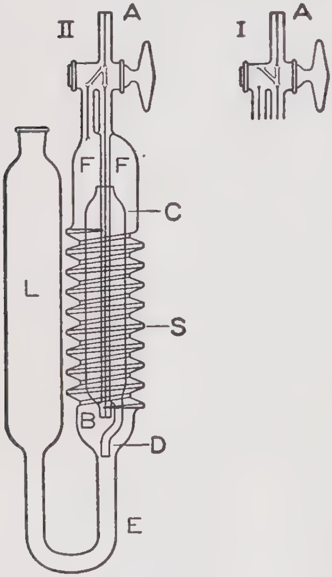

Fig. 42

With the Dennis form of absorption pipette (Fig. 42), both oxygen and carbon monoxide can be removed as completely and as rapidly as is possible with the Hempel absorption pipette in which the gas and absorbent are shaken together.

The rapid and complete absorption is a function of the composition of the reagent as well as the construction of the pipette in which it is to be employed. Anderson[46] has shown that by using a stronger alkaline solution of pyrogallol,[47] the time necessary for the complete absorption of oxygen in air is decreased, and that with this reagent the Orsat pipette is superior to any form in which the gas is made to bubble through the reagent. However, the deposit which forms from this reagent was found to be a source of trouble with any of the pipettes that he tested and this led Anderson to design[48] a pipette in which the formation of the precipitate is not objectional until the reagent has become nearly exhausted.

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[45] Dennis, *Ind. Eng. Chem.*, **4**, 898 (1912).

[46] *Ind. Eng. Chem.*, **8**, 131 (1916).

[47] Anderson, *Ind. Eng. Chem.*, **7**, 587 (1915).

A further error in analyses made with the usual forms of the Orsat apparatus results from the incorrect positions of the measuring burette.[49] After the removal of the absorbable constituents of the gas mixture, the capillary tube that connects the burette with the pipettes remains filled with the combustible residue; consequently, when a portion of this residue is measured off in the burette and is passed to the combustion apparatus through the capillary tube above the pipettes, it will carry with it the combustible gas remaining in that capillary. This difficulty may be avoided by filling the connecting capillary with the confining liquid (water) in the manner suggested by Pfeifer,[50] or more simply by placing the burette between the absorption pipettes and the combustion apparatus in the manner recommended by Hahn.[51]

Since the Orsat apparatus is chiefly employed for the determination by absorption in liquid reagents of carbon dioxide, oxygen, and carbon monoxide, it would seem to be preferable to limit the apparatus to the determination of these three gases and to construct it in such manner as to render it easily possible to connect the burette, when so desired, with suitable special apparatus for the determination of hydrogen and hydrocarbons. The apparatus is thus rendered smaller, more easily portable, and less fragile, and the combustion results, with proper apparatus, will usually be much more accurate than with the imperfect devices contained in the many forms of the Orsat apparatus now upon the market.

A further drawback in the usual forms of Orsat apparatus is to be found in the rubber bulbs that are attached to the level-cylinders of the pipettes to protect the various reagents from the air. These bulbs rapidly deteriorate, and after short use fail to accomplish the purpose for which they are intended.

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[48] Anderson, *Ind. Eng. Chem.*, **8**, 133 (1916).

[49] See Hahn, *J. Gasbel.*, **49**, 367 (1906).

[50] *J. Gasbel.*, **51**, 523 (1908).

[51] *Loc. cit.*

In the hope of remedying some if not all of the defects of the Orsat apparatus that have been enumerated above, Dennis designed the modification shown in Fig. 43.[52]

The burette B has a capacity of somewhat more than 100 cc. and is graduated from a point near the bottom upward to the stopcock J. This stopcock is a three-way stopcock, the position of which is shown by means of a black glass —| fused to its outer surface. The capillary tube connecting J with the pipettes and with the stopcock K has an external diameter of 6 mm. and an internal diameter of one mm. In fusing on the branch capillaries that extend downward to the three pipettes, the internal diameter of the capillary should at no point be much greater than one mm. if the apparatus is properly made. The three absorption pipettes E, F, and G are of the form already described, and are filled respectively with solutions of potassium hydroxide, alkaline pyrogallol, and ammoniacal cuprous chloride. They are connected with the capillary tube from the burette by means of pieces of soft, black rubber tubing of 1.5 mm. thickness of wall, and these rubber tubes are held in place by wire hooks that pass through the blocks behind the joints, and have threaded ends upon which small set screws are placed. This method of attachment renders it easily possible to remove all the glass parts from the frame. Into the open ends of the three level-tubes of the pipettes are inserted one-hole rubber stoppers, and through the openings of these stoppers pass the branch tubes from the tube SS that is 6 mm. external diameter, and one mm. thickness of wall. This tube passes downward and is joined by a piece of rubber tubing to the upper side of the stopcock attached to the cylindrical vessel T which in turn is connected with V by the glass tube shown by the dotted line. After the pipettes have been filled with the several reagents, the stoppers connecting the level-tubes with the tube *SS* are inserted in place and the protecting reservoir *VT* is half filled with water. As the gas is driven over from the burette into the pipette and is drawn back into the burette, the water in *VT* rises and falls, but protects the reagents at all times from contact with the air. The level-bottle *L* is held in place by a clamp when the apparatus is in transport.

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[52] The apparatus is manufactured by Greiner and Friedrichs, Stützerbach in Thüringen, Germany.

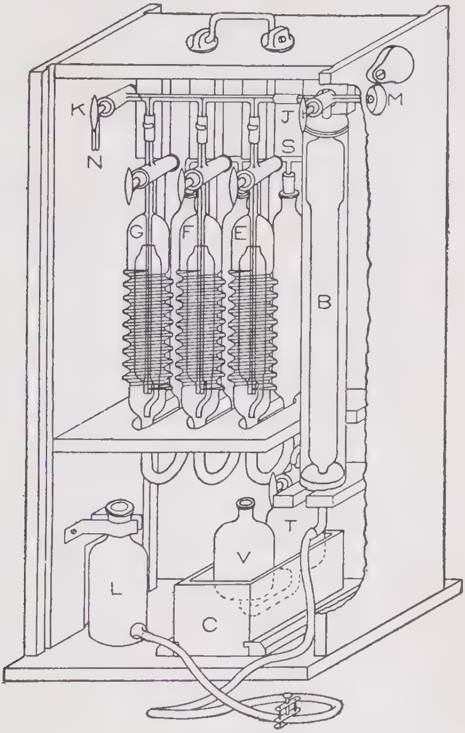

FIG. 43

Manipulation of the Orsat Apparatus.—The level-bottle *L* is filled with water which is then driven up to the top of the burette *B* by turning the stopcock *J* to the position shown in the figure and raising *L*. The stoppers of the level-tubes of the pipettes *E, F* and *G* are then removed and the solutions of the reagents that are to be used in the three pipettes are introduced into the level-tubes. The stopcock *J* is then turned so that the burette *B* is in communication with the capillary tube above the pipettes, and the liquid in each pipette is drawn up almost to the lower side of the stopcock by turning the stopcock to position II, Fig. 42, and lowering the level-bottle *L*. The stopcock of each pipette is closed when the absorbing liquid in it has been raised to this point. Water is now poured into the reservoir *V* until *V* and *T* are half filled. The stoppers attached to the branch tubes of the tube *SS* are then inserted into the necks of the level-tubes of the pipettes.

The stopcock *J* is now turned to the position shown in Fig. 43 and the water in the burette *B* is allowed to run back into the level-bottle *L* and is then poured out of L. The level-bottle is then filled with water that has been saturated with the gas mixture that is to be analyzed (see p. 87), and the burette *B* is filled with this confining liquid up to the mark on the capillary just below the stopcock *J*. The tube *N* is now connected with the pipe or gasometer from which the sample of gas is to be drawn, the stopcock *K* is opened and somewhat more than 100 cubic centimeters of the sample is drawn into the burette *B*. The stopcock *K* is then closed and exactly 100 cubic centimeters of gas is measured off in *B* in the manner described on p. 67, the excess pressure being released by turning *J* to the position shown in the figure. The stopcock *J* is then turned to such position that the burette *B* communicates with the absorption pipette *E*, the level-bottle *L* is raised and the stopcock of the pipette is carefully turned to position II, Fig. 42, and a small amount of gas just sufficient to drive the absorbent downward out of the left hand capillary tube below the stopcock is allowed to enter the pipette. The stopcock is then turned to position I, Fig. 42, and the gas sample is driven over from the burette into the pipette at such speed that the total sample will pass into the pipette in about two minutes. The stopcock of the pipette is then turned to position II, Fig. 42, and the gas, which now occupies the space *FF*, Fig. 42, is drawn back into the burette by lowering the level-bottle, the liquid in the pipette being carefully drawn up into the two capillary tubes below the stopcock until it stands just below the stopcock in each tube. The stopcock is then closed. In the determination of carbon dioxide a single passage of the gas into the pipette suffices for the complete removal of the constituent, and the diminution in volume is read in the burette *B* after the water has been allowed to run down for two minutes. In the absorption of oxygen by alkaline pyrogallol and of carbon monoxide by ammoniacal cuprous chloride, it is necessary to pass the gas twice through the pipette. In such case, by suitable manipulation of the stopcocks, the gas sample after being drawn back from the pipette the first time is immediately passed through it a second time. In the determination of the two gases in question the second passage of the sample may be more rapid than the first (about one minute). The sample is then drawn back into the burette *B* and is measured in the usual manner, the water being allowed to run down one minute before each final reading.

After the absorption of the first constituent in the pipette *E,* the second is absorbed in *F* and the third in *G*. The three gases that are most usually determined with the Orsat apparatus are carbon dioxide, oxygen and carbon monoxide in the order named. The pipette E contains potassium hydroxide (see p. 231), *F* contains alkaline pyrogallol (see p. 174), and *G* is filled with ammoniacal cuprous chloride (see p. 242). The ammonia remaining in the gas after absorption of carbon monoxide by ammoniacal cuprous chloride is absorbed by the water in the burette when the residue is returned to that tube for measurement. If the gas residue contains combustible constituents that are to be determined, the combustion apparatus is connected with the capillary tube *M* and the gas in the burette *B* is driven into the combustion pipette by turning the stopcock *J* to the position shown in Fig. 43 and raising the level-bottle *L*. If only a portion of the residue is to be used for analysis by explosion, the larger part of the gas residue may be passed into the pipette *E*. The smaller portion of the gas that is to be exploded is then measured in *B*, the stopcock *J* is turned to the position shown in Fig. 43 and air is drawn in through *M* until the total gas volume amounts to nearly 100 cc. *J* is then closed, the explosion pipette is connected to *M*, and the mixture of combustible gas and air is driven over into the pipette.

The case containing the apparatus is 57 cm. high, 27 cm. wide and 16 cm. deep. The panels forming the front and back of the case are removed when the apparatus is in use. As illustrative of the uniformity of the results yielded by this apparatus the following analyses of a mixture of carbon dioxide, oxygen, and carbon monoxide may be cited.

	I	II	III	IV
Carbon dioxide, per cent	3.1	3.1	3.2	3.1
Oxygen, per cent	6.0	6.0	5.9	5.9
Carbon monoxide, per cent	22.5	22.6	22.6	22.7

BUREAU OF MINES ORSAT APPARATUS

Burrell and Oberfell[53] have devised a modification of the Orsat apparatus (Fig. 44) for the complete analysis of a gas mixture without connecting or disconnecting any parts. The accuracy of the apparatus is increased by providing the burette with a compensating tube and using mercury as the confining liquid in the burette. The apparatus is somewhat too large to be conveniently portable.

The apparatus consists of a 100 cc. burette *G*, graduated in 0.1 cc., closed at the top by two three-way stopcocks *D* and *C*, and surrounded by a water jacket. The burette is also equipped with a Pettersson compensating tube *H* and manometer *F* for correcting changes of temperature and pressure during the analysis (Chap. VIII). The manometer is filled with mercury or a colorless mineral oil, the latter being used when water is employed as the confining liquid. The burette is connected by a capillary tube to the four pipettes;

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[53] *Ind. Eng. Chem.*, **8**, 228 (1916).

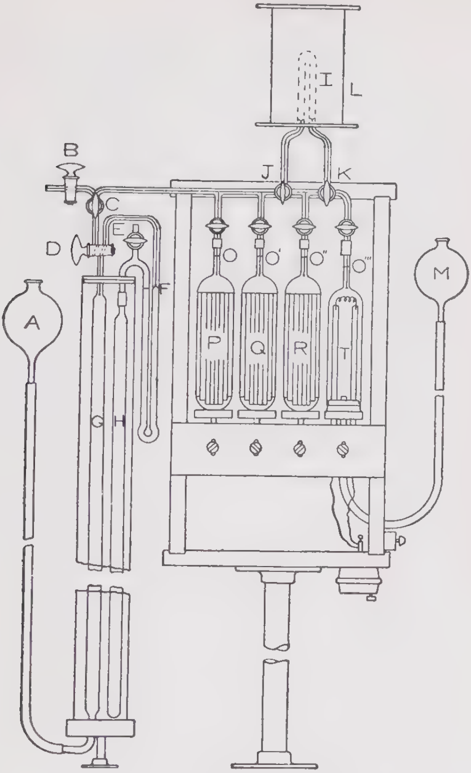

FIG. 44

P for caustic potash, *Q* for fuming sulphuric acid, *R* for alkaline pyrogallol and *T* a pipette for slow combustion. Pipettes *P* and *Q* and *R* are ordinary Orsat pipettes filled with glass tubing for increasing the contact between gas and reagent. The volume of the reagent in each pipette is such that when through the copper oxide tube *I* into the pipette *T* or into the drawn to the marks *O*, *O*′, or *O*″, enough of the solution remains in the rear branch of the pipette to form a seal.

Rubber bags[54] are attached to the rear branches of pipettes *P*, *Q*, and *R* to prevent access of air to the reagents. *I* is a glass tube which contains copper oxide, and which is surrounded by an electrically heated oven *L*. *J* and *K* are three-way stopcocks by means of which the gas can be passed either through the copper oxide tube *I* into the pipette *T* or into the pipette *R*. *A* and *M* are levelling bulbs. The apparatus is also equipped with a rheostat and switch for the electrically heated oven *L*, and a transformer, resistance and switch for the slow-combustion pipette *T*.

Manipulation.—The apparatus is first tested to see that it is gas tight, and the gas in the compensating tube is adjusted to atmospheric pressure. The reagents and the mercury in the combustion pipette are brought to the marks on the capillary tubes, and the manifold and the tube containing copper oxide are washed free of oxygen and residual gas by nitrogen. The sample of gas to be analyzed (about 60 cc.) is drawn into the burette through the stopcocks *B*, *C*, and *D*, first rinsing out the burette with a small portion of the sample (about 20 cc.) to remove residual gas from the connections. The burette is then connected with the compensating tube and the volume of sample is measured. McCollister and Wagner[55] have described a very convenient holder for accurately adjusting the position of the levelling bulb. The gas is then passed four times into pipette *P* to remove the CO_2, six times into pipette *Q* and then into pipette *P* to remove the illuminants, then six to twelve times into *R* to remove oxygen. The gas is then passed twice through the copper oxide tube heated to 275° to 300°, and then into pipette *P* to determine the hydrogen and carbon monoxide. The residual gas is then burned in the combustion pipette *T* with oxygen, and the carbon dioxide that is formed is absorbed in the caustic potash pipette and the methane and ethane determined in the usual manner. A complete analysis with this apparatus will require about one hour.

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[54] The device proposed by Dennis is to be preferred to these rubber bags.

[55] *Ind. Eng. Chem.*, **19**, 86 (1927).

CHAPTER VII

FACTORS AFFECTING THE ACCURACY OF ANALYSES OF GASES

The following factors have a marked influence upon the accuracy of any gas analysis and must be considered in the use and design of an apparatus for this purpose: (1) Specific absorption of the reagent; (2) Change of temperature and pressure during the analysis; (3) Change of water-vapor content of the gas; (4) Solubility of the gases in the confining liquid; (5) Solubility of the gases in the different absorbents; (6) Graduation of the burettes; (7) Capillary error in the apparatus used; and (8) Running down of confining liquid.

1. Specific Absorption of the Reagent.—Hempel[1] proposed the term "analytical absorbing power" as a suitable expression for this property. He determined it by placing one cc. of the reagent in a pipette over mercury, introducing an excess of the pure gas, and shaking it with the reagent as long as rapid absorption takes place. The gas was then passed back into the burette and measured. The decrease in volume thus obtained was divided by four and this value was termed the analytical absorbing power. Anderson[2] has offered the following criticism of this procedure:

"No attempt was made to determine the absolute absorbing power of the reagent nor was the reagent required to remove the gas completely as it must in actual service. The rapidity with which a reagent absorbs a pure gas that is present in excess is quite different from that with which it completely removes the gas from its mixture with other gases. In the first case, the partial pressure of the gas becomes less and less until it equals zero or is so small as to be negligible for technical purposes. In general, as the pressure becomes less, the rapidity of absorption decreases, the last traces of the gas being absorbed with difficulty, or not at all. It is evident. therefore, that the values that are obtained by Hempel's method have little bearing upon the efficiency of the various reagents for quantitative absorptions, and that they afford the analyst no certainty that his reagents may be used until they have absorbed the quantity of gas indicated by Hempel's analytical absorbing power without the possibility of incomplete removal of the constituents."

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[1] Hempel, *Gasanalytische Methoden,* 4th ed., p. 128.
[2] *Ind. Eng. Chem.,* **7,** 587 (1915).

Anderson therefore suggested the "determination of the volume of a gas which a certain reagent will absorb up to the point at which the gas is not completely removed from its mixture with other gases." This value is expressed in the cc. of gas per cc. of reagent, and is known as the "specific absorbing power" or the "specific absorption" of the reagent. He adds that the statement of the specific absorption of a reagent for a gas must contain the name of the apparatus that is employed, the method of manipulation, and the temperature of the reagent, since these conditions affect the results. He further points out that since the specific absorption will be influenced by the percentage of the absorbable constituent that is present, the mixture to be employed in the determination of this value should contain an amount of the absorbable gas not greatly different from that to be expected in the gas mixture to be analyzed. This amount should be given in stating the specific absorption of a reagent.

If a record is kept of the amount of gas that the reagent in a pipette has absorbed, the efficiency of the reagent still remaining in a pipette is always known, and the absorbent can be used to the full extent of its specific absorbing power without uncertainty as to the accuracy of the analysis.

2. Changes of Temperature and Pressure.—When the temperature of a gas rises 1°, the gas expands $\frac{1}{273}$ of its volume at 0° C., provided the pressure does not change (see p. 29).

In other words, a change of 2.7° during a determination will make a difference of about one per cent in the volume. Since an analysis of a gas mixture is actually a series of observations of changes in volume after treatment by different absorbents, the presence of certain constituents might be indicated by a change of temperature when they are really not present. It is, therefore, important either that corrections be made for changes in temperature and pressure when each volume is recorded, or that such temperature variations be avoided by enclosing the burette in a water jacket and making all readings at atmospheric pressure which during the course of a brief analysis may be assumed to be constant. In very accurate work, a compensating tube enclosed in the water jacket surrounding the burette serves to correct for changes in barometric pressure (see Chapter VIII).

3. Change in the Water-Vapor Content (see p. 32).—Variation of temperature will cause a change in the tension of water vapor and precautions must be taken to be sure that the gas is in the same condition at the time of different readings of volume. When the analysis is made over water, the gas will always be saturated with water vapor. When mercury is used as the confining liquid, a film of water on the mercury will keep the gas saturated with water vapor. Like precautions must also be employed with a compensating tube, if it is used.

4. Solubility of Gases in the Confining Liquid.—All gases are soluble to some extent in water, and this solubility may be the cause of large errors in the analysis of gas mixtures, particularly when carbon dioxide, some of the unsaturated hydrocarbons, or gases of high molecular weight are present. One method of lessening the error from this source is to saturate the water with the gas. This may be accomplished by placing the water in a flask, passing the gas mixture through it until the air has been displaced, and then closing the exit tube and shaking the contents of the flask vigorously. Hoffman[3] states that this procedure is not satisfactory because the composition of the gas mixture changes during the analysis. He studied the effect of numerous liquids and found that a 22 per cent solution of sodium chloride dissolved the least carbon dioxide. He also ascertained that the addition of acid [4] to the salt solution is undesirable.[5] A mixture made up of equal volumes of water and glycerol has also been suggested,[6] as has also acidified water. Manchot [7] suggests a method for the determination of the solubility of all the gas constituents in the various confining liquids.

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[3] *Feuerungstechnik*, **14**, 98 (1926).

The error due to solubility of the gases in the confining liquid may, of course, be eliminated by the use of mercury.

5. Solubility of the Gases in the Different Absorbents.—In gas analysis the constituents are removed by suitable absorbents; if combustible gases are to be determined, they are burned to carbon dioxide and water, and one or both of these products is determined (see Chap. XIII). The absorbent may dissolve some of the constituents other than that which it is intended to remove. The physical solubility of the simpler gases such as carbon monoxide, hydrogen, oxygen, nitrogen, and methane is not large, but many of the unsaturated hydrocarbons and saturated hydrocarbons of high molecular weight have a rather high solubility factor.

Errors due to this physical absorption are practically eliminated after several analyses have been made, because the solutions become saturated with the different gases. Consequently when fresh solutions are put into the absorption pipettes, at least three analyses should be made before the results are accepted as correct.

6. Graduation of the Burettes.—Very accurate results can, of course, be secured only if the apparatus for the measurement of gas volumes is correctly graduated. The graduation of a burette by the manufacturer is oftentimes faulty; moreover, one cannot be sure that equal distances on various parts of the scale correspond to equal volumes. For these reasons, the burette should be accurately calibrated throughout its entire length by the user, if high accuracy is desired. This may be done by ascertaining the difference in reading of a liquid meniscus when equal volumes of liquid are withdrawn from the burette at various successive parts of its length. In technical gas analysis, water or aqueous solutions of salt, etc., are used as the confining liquid, but in exact gas analysis mercury is always employed. The burette should, of course, be calibrated with the same liquid which is subsequently to be used as the confining medium.

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[4] Tropsch, *Z. angew. Chem.*, **39**, 401 (1926).

[5] Hoffman, *Z. angew. Chem.*, **39**, 23 (1926).

[6] Burgess and Wheeler, *J. Chem. Soc.*, **97**, 1923 (1910).

[7] *Z. anorg. allgem. Chem.*, **141**, 38 (1924).

In technical gas analysis, where water or some solution which wets the glass is used as the confining liquid, and where the apparatus during the calibration is in the same position as in actual use, the calibration may be made by the same procedure as is generally used for ordinary burettes, in which the Ostwald pipette or the Morse-Blalock apparatus is employed. Another simple method is to compare one burette with another that has been carefully calibrated. A known volume of air is measured off in the calibrated burette, this is then connected to the other burette by an ordinary capillary connecting tube and the air is passed over into the burette and the volume read. Following this procedure the entire length of the burette can be calibrated. The volumes in the two burettes must be measured at the same pressure and temperature.

If such a calibration is made with the burette in an inverted position, a correction must also be made for the meniscus. This correction is subtracted and is given in Table VI, page 92.

If mercury is to be used as the confining liquid, the burette is first thoroughly cleaned and dried, and is then filled with clean, dry mercury. Any air bubbles entrapped between the mercury and the sides of the tube should be removed by applying a strong suction to the top of the burette. The burette is then placed in a vertical position, and an Ostwald pipette of about 2 cc. capacity is attached as shown in Fig. 45.

The burette may be set up in the position in which it is used, but in this case a stopcock should be sealed to the bottom for the calibration, as otherwise the rubber tubing connecting the burette to the pipette may bulge under the pressure of the mercury. If the burette has a stopcock at the top, it is preferable to calibrate it in an inverted position and then to make the necessary meniscus correction.

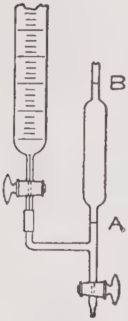

FIG. 45

With the connecting tube completely filled with mercury, and the mercury level in the burette near the 100 cc. mark, the mercury is allowed to run very slowly from the burette into the pipette until it stands at the level *A*. The level of the surface of the mercury in the burette is now accurately read, care being taken to avoid parallax.[8] The mercury is now run slowly from the burette into the pipette until the level of the mercury reaches *B*. The stopcock of the burette is then closed, and the level of the mercury is noted. The mercury in the pipette between the marks *A* and *B* is now run out into a tared weighing bottle and its weight and temperature[9] are determined. The temperature should not vary appreciably during the calibration.

This operation is continued throughout the entire length of the burette, but the weight of the mercury delivered need be determined only three times, once at the start, about the middle, and near the end. The three weights should agree within one part in a thousand; the average is taken for the calculation.

The volume between the marks *A* and *B* (Fig. 45) is equal to

$$g\frac{(1 + 0.00081\,t)}{13.596}\text{ cc.}$$

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[8] A cathetometer should be used for this purpose if extreme accuracy is desired.

[9] If only a relative calibration is desired, no correction need be made for the temperature of the mercury.

where t is the temperature of the mercury and g the weight in grams. The volume between the last calibration point and the stopcock is determined separately by running out this mercury, weighing it, and determining its volume.

When the burette is calibrated in an inverted position, correction for the meniscus error must be made. This is illustrated in Fig. 46, *A* and *B*.

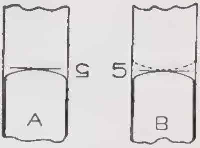

FIG. 46

During calibration the burette is in position *A*, while in actual use it is in position *B*. It will be seen that the actual volume of gas enclosed between the stopcock and the surface of the mercury corresponding to the reading *5* is greater under the actual conditions of use than under the conditions of calibration. In case water is used, the meniscus is of the opposite shape and the correction is subtracted.

The diameter of the tube must be determined. If this cannot be done directly it may be estimated, where great accuracy is not desired, by measuring the outside diameter of the tube and deducting 2 to 3 mm. for the thickness of both walls.

The values for the meniscus correction have been determined by various investigators,[10] and those of Göckel are given in Table VI.

As the zero point is generally in the capillary tube, the meniscus correction for this is small and may be disregarded.

The correct reading for each division of the graduation can now be calculated from the above data and a correction curve or table be made. The temperature correction for the expansion of the glass is very small and is generally omitted.

7. Capillary Error of the Apparatus Used.—In gas analysis there is always the possibility of some of the gas remaining in the capillary tube connecting the burette and absorption pipette and thus not coming in contact with the reagent. This may be eliminated with the Hempel apparatus by proper manipulation (see p. 68), but it should always be borne in mind when such forms of apparatus as that of Orsat are employed (see p. 77). If the capillary space contains an inert gas (nitrogen) before and after the analysis, this error is largely removed. Furthermore, if the gas mixtures which are successively being analyzed do not differ appreciably in composition, the capillary error is largely self-compensating because the gas introduced into the capillaries has about the same composition as that which is removed, and the gases gained and lost in the capillaries as the analysis progresses are relatively the same.

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[10] Bunsen, *Gasometrische Methoden*, 2d ed., p. 38; Winkler, *Zeit. anal. Chem.*, **40**, 403 (1901); Göckel, *Z. angew. Chem.*, **16**, 49 (1903); Winkler, *ibid.*, **16**, 718 (1903).

TABLE VI

Diameter of Tube mm.	Double Meniscus Correction (cc.)	
	Mercury	Water
1	.0026	.0021
2	.0052	.0043
3	.0090	.0093
4	.0128	.0144
5	.0200	.026
6	.027	.039
7	.035	.062
8	.043	.084
9	.056	.114
10	.068	.144
11	.080	.190
12	.091	.236
13	.104	.263
14	.118	.291
15	.140	.343
16	.162	.395
17	.174	.443
18	.185	.492
19	.181	.520
20	.177	.548
21	.180	.605
22	.182	.663
23	.179	.708
24	.176	.754
25	.173	.800

8. Running-Down of the Confining Liquid.—It is of importance, if accurate results are desired, that the confining liquid over which the gas is measured be allowed to flow down the walls of the burette in exactly the same manner and for the same length of time after each absorption. If the tube of the Hempel burette is clean, the running-down of water is practically complete in three minutes. If the burette is allowed to stand two minutes longer, the meniscus will stand from 0.02 to 0.03 cc. higher than after three minutes, a difference that is negligible in technical gas analysis with water as the confining liquid. In the description of the manipulation of the apparatus on page 67 it is stated that the water should be allowed to run down for one minute. The results will naturally be more accurate if the three-minute interval is employed, but for technical analyses where speed is a desideratum and great accuracy is not necessary, much time may be saved by making the readings only one minute after the gas has been passed back into the burette.

In apparatus in which gas volumes are read over liquids other than water or mercury, such as solutions of fixed alkalies, cuprous chloride, alkaline pyrogallol, and the like, the running-down of the liquid takes place slowly, and an error in measurement of one cubic centimeter or more may result if the reading is not made under exactly the same conditions in all cases. While distilled water will run down completely in a Hempel burette in five minutes, a five per cent solution of sodium hydroxide requires ten minutes, and concentrated sulphuric acid from fifteen to twenty minutes. If in an analysis of a gas mixture the residual gas volumes are read first over one liquid and then over another, it is apparent that rapid and at the same time accurate work is almost if not quite impossible.

CHAPTER VIII

THE HEMPEL APPARATUS FOR EXACT GAS ANALYSIS WITH MERCURY AS THE CONFINING LIQUID

The solubility of gases in water precludes great accuracy when this substance is used as the confining liquid, even when it is saturated with the gas mixture that is being analyzed. If very accurate results are desired, mercury must unquestionably be employed as the confining liquid.

The simple and exact gasometric methods proposed by Bunsen do not admit of the rapid performance of a large number of exact analyses. In the method devised by Doyère,[1] the gas, saturated with moisture, is measured in a Bunsen eudiometer and the necessity of correction for pressure is avoided by joining the eudiometer with an iron holder having a screw attachment by means of which the mercury in the tube and in the suitably formed trough may be brought to the same level. Doyère used a separate pipette for each reagent. Hempel[2] modified Doyère's method of measurement and changed the construction of the necessary absorption pipettes, and developed a procedure which makes possible rapid and very exact determinations without the use of delicate physical instruments. Bunsen measured the gases under varying pressure and varying volume, Doyère measured them under constant pressure and varying volume, while Hempel measured them under constant volume and varying pressure.

The need for these earlier processes was due to the fact that at that time it was difficult to obtain glass stopcocks that were perfectly tight. The manufacture of glass apparatus has been so improved that satisfactory instruments can now easily be procured, and consequently these older processes have fallen into disuse. The present methods of exact gas analysis are merely more accurate forms of those used in technical analysis. The burettes are graduated with greater precision, mercury instead of water is used as the confining liquid, and corrections are made for the variations of the temperature and the pressure of the gas during analysis. Complete certainty that the apparatus is absolutely tight is, however, assured only by the use of apparatus that contains no stopcocks or rubber connections whatever, and in which all joints are made by fusing the glass tubes together.

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[1] *Ann. chim. phys.*, [3] **28**, 1 (1850).

[2] Dennis, *Gas Analysis* (1913), p. 101.

I. GAS BURETTES WITH CORRECTION FOR VARIATIONS IN TEMPERATURE AND BAROMETRIC PRESSURE

Pettersson [3] was the first to show that by means of a tube inclosing a volume of gas, it is easy to compensate the errors that would result from variations in temperature and in the pressure of the atmosphere. Extreme accuracy in gas analysis can be attained by the use of such apparatus, the results being quite as exact as those obtained with the more elaborate apparatus for exact analysis of Doyère and Hempel, provided always that the stopcocks and rubber connections are perfectly tight. In the different forms of gas apparatus with temperature and pressure correction, the measuring tubes are varied to accommodate gas volumes of different sizes. Fig. 47 shows the apparatus intended for the measurement of gas volumes up to 100 cc. Others may conveniently be used when the gas volume amounts to about 150 cc., and for the examination of gases evolved from bacteria, the gas volumes here usually not exceeding 10 cc.

The instrument consists of the graduated measuring tube *A*, the correction tube *B*, the manometer tube *F*, and the level-bulb *G*. The measuring tube and level-bulb are mounted in suitable iron feet. The measuring tube and the correction tube stand in the wide glass cylinder *C*, which is filled with water to insure that these two tubes are at all times at the same temperature. The measuring tubes are closed at the top by a three-way glass stopcock.

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[3] *Z. anal. Chem.*, **25**, 467 (1886).

The correction tube *B* and the manometer tube *F* are made from plain glass tubes fused together in the form shown in the cut. *H* is a small capillary tube which in some forms is equipped with a stopcock. The manometer tubes are U-shaped, and are somewhat widened at *K* and *I*, these two widened portions having marks scratched on the glass at exactly the same height. The manometer tube is joined to the measuring tube by means of a piece of rubber tubing connecting the end of the capillary *L* with the tube *E* of the stopcock. The reason for making the manometer tube so long lies in the fact that otherwise, if the apparatus is carelessly handled, the mercury might easily be driven from the manometer tube into the burette or the correction tube. With the arrangement shown in the figure this is almost impossible, since the difference in pressure must be more than half an atmosphere before the mercury can pass over into either tube. The manometer tube is made completely of glass to prevent the mercury being contaminated with the dirt from the interior of a rubber connection. If the burette has become dirty, the manometer tube is removed, and the rest of the instrument may then be cleaned without danger of any change taking place in the gas volume inclosed in the correction tube.

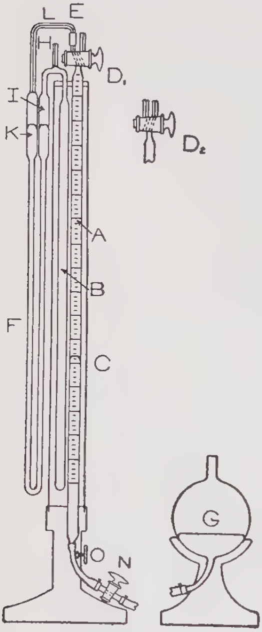

Fig. 47

To prepare the apparatus for use, draw some distilled water through the capillary *H* into the correction tube *B*, and also moisten the walls of the measuring tube *A* with a drop or two

Gas

of water. Fill the level-bulb *G* with mercury, and turn the glass stopcock to the position shown in D_1. Then by raising the level-bulb drive the mercury over into the manometer tube until the latter is filled up to the marks on *K* and *I*.

Before proceeding with the analysis, the volume of the manometer tube from the mark on *K* to the point *E* must be ascertained. To do this, draw over the mercury in the manometer until it reaches *E*, then turn the stopcock *D* until it has the position of D_2, and now draw any desired volume of air into the burette. Leaving the stopcock open, read off this volume of air on the scale of the burette, the air here being, of course, under the prevailing pressure of the atmosphere. Turn stopcock *D* so that the burette communicates with the manometer tube, and drive the air over into this latter tube until the mercury in it stands at equal height in its two branches; that is, at the marks on *K* and *I*. The difference between the two readings on the measuring tube, provided the tube *H* remains open, gives the volume of the manometer from the mark on *K* up to *E*.

Correction tube *B* may be used in either of two ways. We may inclose within it an indeterminate amount of air by simply fusing together the end of the tube *H* so that the volume in the correction tube will correspond to the barometric pressure and temperature prevailing at the time of operation, or we may fill *B* with such an amount of air that the apparatus will indicate directly gas volumes reduced to standard conditions—that is, to 0° C. and 760 mm. pressure. In the latter case, the gas will have at the ordinary temperature of the room a pressure somewhat above that of the atmosphere. In the former case the barometer and the thermometer must be read at the time the tube *H* is fused together, so that we may be able to correct gas volumes whenever this is necessary.

In many cases it is highly desirable to so arrange the apparatus that the reading on the measuring tube *A* corresponds directly to volumes at 0° C. and 760 mm. pressure. To accomplish this a piece of rubber tubing is slipped over the end of the capillary tube *H* and fastened firmly in place by a wire ligature. By lowering the level-bulb, mercury is drawn over into the manometer tube until it reaches the capillary *L*, and the burette is then allowed to stand for two hours in a room of fairly constant temperature. The stopcock *D* is then opened so that the contents of the burette are in free communication with the atmospheric air. As soon as one is convinced that all parts of the apparatus are at the same temperature, the gas volume in the burette is read exactly, and the temperature and barometric pressure are noted. The thermometer and barometer should stand in the same room with the apparatus. The stopcock *D* is closed and the volume of the gas at standard conditions is now calculated.

Example.—The gas volume is 97 cc., the barometric pressure 753.3 mm., and the temperature 8.75° C. The space from *K* to *E* in the manometer has previously been determined and found to be 1.8 cc. The tension of the water vapor at 8.75° C. is 8.4 mm. The corrected volume is 92.1 cc.

Since, however, in making measurements with the correction tube, the gas fills the space from *K* to *E*, this volume must be subtracted from the above result:

$$92.1 - 1.8 = 90.3 \text{ cc.}$$

In order now to adjust the gas volume in the correction tube so that readings of volumes in the burette will be reduced at once to standard conditions, the stopcock *D* is turned so that the burette communicates with the manometer tube, and the gas in the burette is compressed by raising the level-bulb *G* to the volume which it has been calculated that it would occupy at 0° C. and 760 mm. pressure. The mercury in the manometer tube is, of course, forced out of equilibrium by this operation. Air is now blown into the correction tube through the rubber tube at *H* until the mercury stands at the same height in the two branches of the manometer tube, and the rubber tube is then closed by means of a strong pinchcock placed directly above the end of *H*.

A rubber tube cannot remain tight for any length of time, and therefore the glass tube *H* must be fused together. This cannot be done at once because of the high pressure of the air in the correction tube, but the operation may easily be performed by first removing the rubber tube joining the manometer tube with the burette at *E* and then placing the correction tube *B* in a freezing mixture of salt and ice, allowing it to stand therein until the mercury in the manometer shows that the pressure on the inside of the correction tube is smaller than that of the external atmosphere. The tube *H* can now be heated by means of a blast lamp and drawn out and fused together directly below the rubber tube which is upon it.

There is danger that the glass tube *H* may crack when it is heated. This can be avoided by painting it with a thin emulsion of Plaster of Paris stirred up with water, leaving the place where the tube is to be drawn out uncovered by this coating. The Plaster of Paris offers an excellent protection against the overheating of that part of the glass tube which it is not desired to soften and can afterward easily be removed with the aid of water.

The correction tube, after being thus adjusted, is again joined to the burette. The readings of gas volumes in the burette now give directly the volumes under standard conditions, no matter how great may be the variations of temperature and pressure, provided always that in making the measurements the stopcock is turned to the position of D_1 and the mercury in the manometer tube is brought to the marks *K* and *I* by expanding or compressing the gas in the measuring tube. The exact adjustment of the mercury in the manometer tube is effected by raising or lowering the level-bulb *G* until the mercury stands nearly at the marks *K* and *I*, then closing the stopcock *N* and turning the screw *O* so as to exert greater or less pressure on the piece of rubber

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tubing against which it plays. This piece of rubber tubing, as is shown in the figure, connects the lower end of the burette with the stopcock *N*. In this manner the surface of the mercury in the two arms of the manometer may be brought exactly to the same level. This style of adjustment is original with Pettersson and enables us to effect slight changes in the size of the gas volume in a most convenient and rapid manner. In all cases where rubber tubing must withstand considerable pressure it is desirable to use a special rubber tubing,[4] which, although not quite so elastic as the ordinary kind, will easily withstand a pressure of several atmospheres.

The Pettersson type of correction tube is used by Ott[5] in an apparatus for exact analysis of his own design.

White[6] has described a bulbed gas burette for exact gas analysis with a modified stopcock and Pettersson correction tube. This was devised to correct for the inaccuracy of reading the gas volumes, and to avoid the possibility of the inclusion of air and the leakage of gas while making connections to the pipettes, which are possible causes of error with the usual form of burette. Gregg[7] has suggested a modification of the correction tube to make the adjustment of the height of the mercury in the compensating tube more rapid, more accurate, and less bothersome to the operator. The usual method of adjusting the mercury level by bringing it to a mark on the glass tube as replaced by two platinum wire contacts which are so inserted in the tube that when the mercury reaches the desired level a miniature lamp is lighted. Weaver and Ledig[8] have described a weight burette using this type of compensating tube for the measurements of gas volumes requiring greater precision than can easily be obtained with the ordinary burette. A volume of mercury equal to the volume of gas introduced is displaced from the measuring bulb, and the volume of gas is calculated from the weight of the mercury displaced.

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[4] This is a smooth black, so-called ''varnished'' tubing which withstands heavy pressure without reinforcement.

[5] *J. Gasbel.*, **63**, 198 (1920); *Gas u. Wasserfach*, **68**, 367 (1925); **69**, 289 (1926).

[6] *J. Amer. Chem. Soc.*, **22**, 343 (1900).

[7] *Ind. Eng. Chem.*, **9**, 528 (1917).

[8] *J. Amer. Chem. Soc.*, **42**, 1177 (1920).

A further modification of the Pettersson compensating tube has been suggested by Vilbrandt,[9] and is shown in Fig. 48. The manipulation of this form is the same as that of the original type, but the tube possesses the advantage of being entirely enclosed in the water jacket. It is simple to construct and manipulate, and is not fragile.

II. THE ABSORPTION PIPETTES

On account of the great differences in pressure caused by columns of mercury of only moderate height it becomes necessary to give to these absorption pipettes, which are partially filled with mercury, a form somewhat different from that adopted for the pipettes containing aqueous solutions.

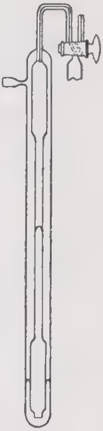

FIG. 48

The Simple Mercury Absorption Pipette

This consists of two bulbs, *A* and *B*, Fig. 49, joined together by a piece of varnished rubber tubing. The bulb *A* has a capacity of about 130 cc. and *B* a capacity of about 150 cc.

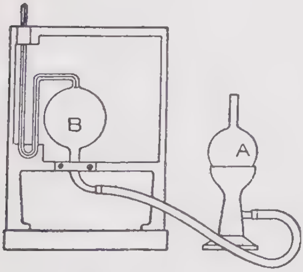

FIG. 49

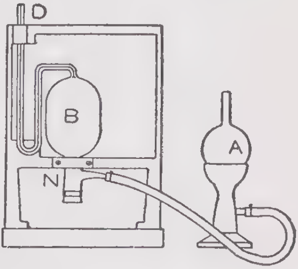

FIG. 50

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[9] *Ind. Eng. Chem.*, **16**, 936 (1924).

The Simple Mercury Absorption Pipette for Solid and Liquid Reagents

This resembles the pipette just described, except that the bulb *B*, Fig. 50, is cylindrical in form and has at its lower extremity a cylindrical neck, *N*, through which the bulb can be filled with solid substances. *N* is then closed with a cork or rubber stopper held in place by a wire ligature.

The Mercury Absorption Pipette with Absorption Bulb

This pipette has in addition to the two bulbs *A* and *B*, Fig. 51, a third bulb *C* filled with broken glass or with glass beads. The advantage of this small bulb lies in the fact that when the gas is driven over into the pipette, the reagent which the latter contains clings to the small pieces of glass in *C*, and causes a more complete absorption of that constituent of the gas mixture which is to be removed. The pipette has, however, one drawback: with viscous reagents bubbles of gas are liable to cling to the broken glass in *C*.

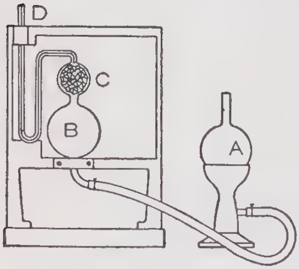

Fig. 51

The mercury pipettes are manipulated in exactly the same manner as the pipettes for aqueous solutions already described, except that here only small quantities of the reagent are employed in order to reduce the error that is caused by the solubility in the reagent of those gases which are not directly absorbed by it. This error can be still further lessened by introducing into the gas pipette an amount of reagent sufficient for two analyses of the gas mixture in question. In the first analysis the reagent becomes saturated with those gases for which it is not an absorbent, and the error due to solution of the gases in the reagent is thus minimized in the second analysis. The reagents are introduced into the gas pipette by means of a small pipette inserted in the rubber tube at *D*.

Bone and Wheeler's Apparatus (Fig. 52)

This apparatus,[10] a modification of that earlier described by Bone,[11] was designed for use in a commercial research laboratory.

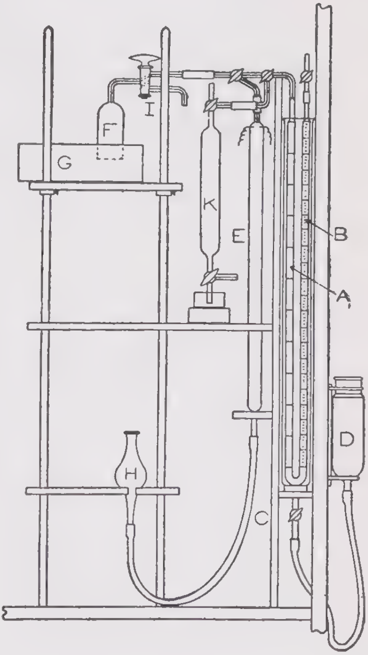

FIG. 52

The apparatus consists essentially of: (1) a water-jacketed combination of measuring and pressure tubes, *A* and *B*, connected through the stopcock *C* with the mercury reservoir *D;* (2) an absorption vessel *F* standing over mercury in the trough *G;* and (3) an explosion tube *E* connected with a separate mercury reservoir *H*. All of the connections are of capillary tubing with stopcocks where they are necessary, and the complete analysis is carried out over mercury. The gas sample is introduced from the sample tube *K* into the measuring tube *A*. The sample is then measured by measuring the pressure of the gas at constant volume. For this purpose the gas is brought to a certain "constant volume" mark in the measuring tube *A* and its pressure is read off on the tube *B*. From 2 to 5 cc. of the reagent to be used is introduced into the absorption vessel by means of a pipette inserted below the surface of mercury in the trough. The gas sample is then brought into contact with the reagent in the absorption vessel *F*, is then returned to *A*, and the decrease in pressure is noted. The reagent is then removed from *F* through the stopcock *I*, the absorption vessel is rinsed, and the next reagent is introduced. After all of the absorbable constituents are removed, the residue is mixed with oxygen and is burned in tube *E*. With this method of measurement, small volumes of gas may be used for the analysis, and the measurements are independent of the barometric pressure and are unaffected by the tension of aqueous vapor.

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[10] *J. Soc. Chem. Ind.*, **27**, 10 (1908).
[11] *Proc. Chem. Soc.*, **14**, 154 (1898).

Numerous modifications of this apparatus have been proposed by Balcon,[12] Taylor,[13] Smith,[14] Blair and Wheeler,[15] and Saunders.[16]

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[12] *J. Gas Lighting*, **121**, 102 (1913).
[13] *Ind. Eng. Chem.*, **6**, 845 (1914).
[14] *Gas World*, **71**, 342 (1919).
[15] *J. Soc. Chem. Ind.*, **41**, 187 (1922).
[16] *J. Chem. Soc.*, **123**, 2826 (1923).

CHAPTER IX

THE CONSTRUCTION AND CONNECTION OF APPARATUS

Glass Blowing.—It is of great convenience to the gas analyst to be able to make simple forms of glass apparatus and to repair broken parts. The elements of glass blowing are clearly described in such books as those by Shenstone, Frary, and Waran, and with practice it is possible for almost every chemist to develop considerable facility in glass blowing.

The blast-lamp should have cocks on the lamp itself for the easy regulation of the supply of gas and air blast. It should give with full blast pressure a colorless flame about thirty cm. long, and with diminished blast pressure a yellow-tipped flame about forty cm. long. On cutting down the gas and air pressure, the lamp should furnish a small, sharp-pointed, colorless flame about five cm. long.

The glass tubing should be easily fusible and the ordinary sizes, from six mm. to twenty mm. in diameter, should have a wall about one mm. thick. Glass tubes or glass parts that are to be fused together should be of the same kind of glass, for joints made of different kinds of glass will usually easily break apart. All joints should be highly heated and thoroughly blown out, and should be carefully annealed by holding them in the luminous flame of the lamp until they are thoroughly coated with soot and then allowing them to stand until cold.

Amateurs that have difficulty in blowing glass bulbs in the middle of tubes will find it convenient to order from a glass manufacturer a supply of thin walled glass bulbs, of from four cm. to seven cm. in diameter, with side tubes of from seven mm. to twelve mm. external diameter and each about fifteen cm. long.

Since some find difficulty in properly bending capillary tubing for the Hempel apparatus, it may be stated that such tubing, which should be six mm. external diameter with one mm. bore, may easily be bent, without blowing, by first warming it carefully in the luminous flame of the blast lamp, and then heating the spot at which the bend is to be made in a blast flame about two cm. wide, turning the tubing during the heating. As soon as the tube softens, it is bent directly to the desired angle as one would bend a piece of glass rod.

Mounting of Apparatus.—If glass apparatus is to be mounted on a frame or standard, it should be fastened at only a few places so as to allow of as free expansion as possible, and it is best secured in position by fastening to the support a metal band that passes around the glass tube, but does not touch it, and then filling the intervening space between the metal strap and the tube with Plaster of Paris.

Rubber Connections.—If glass tubes are to be joined together by rubber tubing, the ends of the tubes should be rounded in the flame, and should be brought close together within the piece of rubber tubing. To secure the rubber tubing in place, it may be fastened by wire ligatures. For this purpose copper wire about one mm. in diameter is most suitable. Each ligature should consist of only one turn of the copper wire around the tube, the ends being drawn and tightly twisted together by means of a pair of pliers. Long rubber connections should be avoided, not merely because the rubber tubing is somewhat porous, but also because air in the tube adheres tenaciously to the walls. A rubber connection cannot be relied upon to be gas-tight over a long period of time, and the tubing should frequently be examined, and should be renewed when it shows deterioration. A rubber connection may be made gas-tight by surrounding it with a mercury seal as shown in Fig. 53.

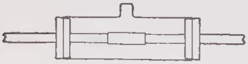

Fig. 53

A rubber tube capable of withstanding high pressure is needed in connecting level-tubes or level-bulbs with gas burettes when the apparatus is to be filled with mercury as the confining liquid. The so-called "varnished" rubber tubing,[1] about six mm. internal diameter and with a wall two mm. thick, is very suitable for this purpose. For connecting the level-bulb of a mercury air pump with the pump, the "varnished" rubber tubing should be about 12 mm. internal diameter and 2.5 mm. thickness of wall. This tubing is superior to the ordinary pressure rubber tubing with very thick wall, because its larger internal diameter permits free flow of the mercury, and its smooth interior surface avoids the fouling of the mercury by particles of the rubber. It has been found in practice that it will easily withstand a working pressure that rises at times to five atmospheres.

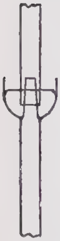
FIG. 54

Mercury Seals.—For making a gas-tight connection which may easily be taken apart, the use of mercury seals, shown in Figs. 54 and 55, are very convenient. Von Antropoff[2] suggests covering the mercury with sealing wax or replacing the mercury entirely by sealing wax or some other solid of relatively low melting point, while Carroll[3] says that if the mercury is covered with a thick film of celluloid or collodion it may then be used in a horizontal or inverted position.

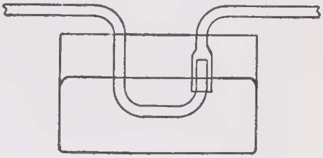
FIG. 55

Ground-Glass Joints.—Ground-glass joints are very convenient in such investigations of gases as necessitate the detachment of a part of the apparatus, for their manufacture has now been so perfected as to render them gas-tight. "Normal" ground-glass joints,[4] which are interchangeable, are extremely useful in cases where a bulb or tube is to be detached from the chain of apparatus, and joined to it at some other point.

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[1] See p. 100.

[2] *Ber.*, **56**, 2137 (1923).

[3] *Nature*, **113**, 858 (1924).

[4] These may be obtained from Greiner and Friedrichs, Stützerbach in Thüringen, Germany.

Glass to Metal Joints.—McKelvy and Taylor[5] have reviewed the work that has been done on this subject and have described in detail the methods used by the Bureau of Standards for making both soldered and fused joints. The soldered joints are made by first platinizing the glass tubing, then copper plating it and soldering to the metal. Dundon[6] was unable to make satisfactory joints by the above soldering method between copper and glass with tubing more than 8 mm. in diameter, and he recommends an electro-deposition of copper between the platinized glass tube and the metal. However, Myers[7] states that the soldered joints are satisfactory on tubing up to 41 mm. in diameter. Ridyard[8] has suggested a method of coating the glass with a lead film and then soldering to the metal, and he states that such a joint will maintain a vacuum up to 10^{-4} mm. at 150° for several days.

Stopcocks.—Hollow-blown stopcocks are so perfectly made that they may be employed with very slight danger of leakage provided they are properly lubricated. The form of stopcock shown in Fig. 56 and Fig. 57 is superior to the stopcock with straight bore because it avoids the danger of leakage due to the channeling of the barrel of the stopcock.

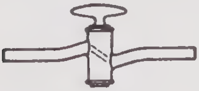

FIG. 56

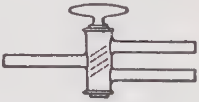

FIG. 57

As a special precaution against leakage of gas, the mercury sealed stopcocks may be used.

Lubrication of Stopcocks.—An excellent preparation for the lubrication of glass stopcocks that does not deteriorate on

[5] *J. Am. Chem. Soc.*, **42**, 1364 (1920).
[6] *J. Am. Chem. Soc.*, **45**, 716 (1923).
[7] *J. Am. Chem. Soc.*, **45**, 2135 (1923).
[8] *J. Am. Chem. Soc.*, **46**, 287 (1924).

keeping, does not work out at the ends of the key, and gives off no hydrocarbon vapors may be made as follows: Place in an evaporating dish twelve parts of vaseline and one part of paraffin wax. Heat this mixture over a Bunsen flame and maintain the contents of the dish at a temperature that will keep the materials fluid but will not cause the mixture to emit fumes. Drop in successive portions of soft, black-rubber clippings and stir the mixture after each addition until the rubber is completely dissolved. After about nine parts by weight of rubber has been added, take out a small sample of the lubricant on the end of a stirring rod, allow it to cool, place it on the ball of the thumb, squeeze it with the end of the middle finger and then rapidly tap the finger upon the thumb at the point covered by the lubricant. If on this treatment the lubricant forms light feathery particles that float off in the air in fine flocks the proper mixture has been reached. If the lubricant does not behave as described, stir in more rubber and test again. About ten parts by weight of the rubber will usually be required for the above amounts of vaseline and paraffin.

All vapors and dissolved air may be removed by melting the above lubricant in a closed container and keeping the enclosed space evacuated until all the vapors and air have escaped from the material, and then allowing it to solidify before opening to the air.

Noyes and Shepard[9] suggest the use of equal parts of black rubber, vaseline, and paraffin wax.

In lubricating a glass stopcock, the key and barrel should first carefully be cleaned and then the thinnest possible film of vaseline be rubbed over the surface of the key of the stopcock. The lubricant is then rubbed over the key, which is next inserted in the barrel and turned around until the lubricant is evenly distributed over the surface.

In the Cornell laboratory, it has been found that a Greiner and Friedrichs stopcock of the form shown in Fig. 56, when lubricated with this mixture, will withstand a pressure of four atmospheres on one side and a Torricellian vacuum on the other for a considerable length of time without any leakage whatsoever.

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[9] *J. Am. Chem. Soc.*, **20**, 345 (1898).

Another recipe for a lubricant for stopcocks is given by Keyes:[10] 26 grams of paraffin (melting point 70°) is placed in a dish and heated until it melts, and then 18 grams of pure gutta percha is added in small amounts at a time, the temperature of the mass being held at about 150° until the gutta percha is dissolved. 20 grams of a heavy mineral oil such as is supplied with the Fleuss pumps is then added, and the mixture is maintained at a temperature of from 125° to 130° for from four to five hours. Bradley and Wilson[11] have given receipes for many different types of lubricants.

If the gases or liquids that are to pass through the stopcock are of such nature as to cause them to attack the rubber lubricant, metaphosphoric acid may be used. The key and barrel of the stopcock are thoroughly cleaned and dried; the key is dipped into phosphorus pentoxide, is allowed to stand in the air until the pentoxide has taken up sufficient water to form metaphosphoric acid, and is then inserted into the barrel and turned until the metaphosphoric acid is spread evenly over the surface.

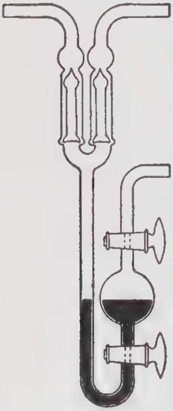

FIG. 58

Stopcocks lubricated in this manner are, however, very apt to stick unless they are frequently turned.

Mercury Float Valve.—Certain gases have a chemical action upon the lubricant used in stopcocks; to overcome this difficulty Stock[12] has designed a floating valve (Fig. 58) which is free from this difficulty. It consists of a pair of narrow tubes containing two glass floats which are carefully ground into their seats. The floats are raised and lowered by the mercury in the attached U-tube.

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[10] *J. Am. Chem. Soc.*, **31**, 1271 (1909).

[11] *Ind. Eng. Chem.*, **18**, 1279 (1926).

[12] *Ber.*, **47**, 3112 (1914); *Z. Elektrochem.*, **23**, 33 (1917); Dennis, Corey, and Moore, *J. Amer. Chem. Soc.*, **46**, 657 (1924).

When the apparatus is under diminished pressure, a valve may be closed by opening the two stopcocks and admitting air or opened by applying suction to the side arm. Stock[13] has also suggested the use of porous plates in place of the glass floats.

[13] *Ber.*, **58**, 2058 (1925).

CHAPTER X

PURIFICATION OF MERCURY

Mercury that is pure will pass over a glass surface without adhering to it or leaving a deposit upon it. If the mercury is contaminated with other metals there forms upon the mercury a layer of oxides that adhere to glass. Commercial mercury frequently contains zinc and lead, and through use in the laboratory it usually soon becomes contaminated with copper. These foreign metals may be removed by oxidizing them and then dissolving their oxides with an acid that does not attack the mercury. They may also be separated from the mercury by bringing the impure metal into contact with a mercurous salt and a free acid, which will remove from the mercury such metals as stand above it in the electromotive series, the foreign metals passing into the solution and precipitating an equivalent amount of mercury. Metals that stand below mercury in the electromotive series, such as platinum and gold, cannot be separated from the mercury in this manner. In such case it is best to distill the mercury under diminished pressure. It was formerly supposed that certain metals, such as zinc, would distill over with the mercury, but Hulett has shown[1] that this does not take place if bumping of the mercury during distillation is avoided. He has ascertained, however, that when the mercury is contaminated with dry metallic oxides, these oxides may be carried over with the mercury vapor.

If the mercury is very impure a considerable portion of the dirt and oxides may be removed by running the mercury through a dry filter paper that is folded and placed in a glass funnel in the usual manner, with a hole one to two mm. in diameter in the tip of the filter. The mercury may also be filtered through leather,[2] bamboo,[3] cloth,[4] chamois,[5] silk,[6] or Jena glass filters.[7] The metal may then further be purified by one or more of the processes described below.

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[1] *Z. phys. Chem.*, **33**, 611 (1900).

Purification of Mercury by Nitric Acid.—If the mercury is contaminated with other metals, it may rapidly be freed from a considerable portion of them by placing it in a bottle, covering it with a layer of a five per cent solution of nitric acid, or with a solution of mercurous nitrate to which a little nitric acid has been added, and then blowing air through the mercury through a glass tube. If air blast is not available, the mercury and acid may be placed in a filtering flask into the neck of which is inserted a one-hole stopper carrying a glass tube reaching nearly to the bottom of the flask. Upon connecting the side arm of the flask with a suction pump, air will be drawn down through the tube and through the mercury. Dixon and McKee[8] have described an apparatus which may be used for the above procedure or for Bettel's[9] cyanide method. Many other methods have been proposed. These include the use of ferric chloride,[10] dilute sulphuric acid and potassium dichromate,[11] hydrochloric acid,[12] steam distillation,[13] oxygenated charcoal,[14] and air.[15] The removal of base metals by this latter method is incomplete.[16]

Further purification of the mercury may then be effected by the method of Meyer[17] in which the mercury is passed in a fine stream through a long column of dilute nitric acid using the apparatus shown in Fig. 59.

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[2] Bolton, *Z. Electrochem.*, **2**, 76 (1896); Dunnicliffe, *Chem. News*, **116**, 41 (1917).

[3] Karsten, *Z. Instrumentenk.*, **8**, 135 (1888).

[4] Hildebrand, *J. Am. Chem. Soc.*, **31**, 933 (1909).

[5] Moore, *ibid.*, **32**, 971 (1901).

[6] Patten and Mams, *Ind. Eng. Chem.*, **9**, 960 (1917).

[7] Booth and Jones, *ibid.*, **19**, 104 (1927).

[8] *J. Chem. Soc.*, **123**, 895 (1923).

[9] *Chem. News*, **97**, 158 (1908).

[10] Ulex and Wild, *Ann.*, **25**, 222 (1838).

[11] Brühl, *Ber.*, **12**, 204, 576 (1879).

[12] Dunstan, *Phil. Mag.*, [5] **29**, 367 (1890).

[13] Violette, *Compt. rend.*, **31**, 546 (1850).

[14] Forbes, *Chem. News*, **106**, 74 (1912).

[15] Crafts, *Bull. soc. chim.*, **29**, 856 (1888); Dixon and McKee, *loc. cit.*

[16] Hulett, *Phys. Rev.*, **33**, 312 (1911).

[17] *Z. anal. Chem.*, **2**, 241 (1863).

A is a 2 cm. glass tube about 55 cm. long, with an opening 4 to 5 cm. wide at the top and sealed at the bottom to a capillary bent glass tube *D*. *B* is either a large funnel fitted with a filter, or a separatory funnel. The lower end is drawn down to a small opening. The indentations in the side of *A* extend from a quarter to half-way across the tube. Some pure mercury is first poured into the tube *D*, and *A* is then filled with 5 per cent nitric acid, the acid being kept in the tube by the mercury in *D*. Upon allowing the mercury to drop from *B*, the purified metal passes slowly over into *C*. Hildebrand [18] covers the tip of the funnel *B* with muslin to break the mercury up into numerous fine streams. Desha [19] has modified the apparatus to automatically raise the mercury and keep it in continuous circulation, and Loomis and Acree [20] have combined with this an electrolytic purification in which the mercury is made the anode in dilute nitric acid.[21] Patten and Mains [22] have further modified this method by providing for the automatic renewal of the nitric acid.

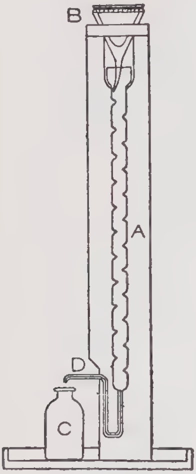

FIG. 59

Purification of Mercury by Concentrated Sulphuric Acid and Mercurous Sulphate.—This is a very simple and efficient method which yields mercury that is both dry and of fairly high purity, but is less satisfactory than the treatment with nitric acid.

The process of purification may conveniently be carried out in a heavy separatory funnel of from 2 to 4 liters capacity, the funnel being supported in a wooden stand at such a height that an ordinary bottle may readily be brought under its lower end. The funnel is first partly filled with mercury (impure mercury may be used here, if no purified mercury is at hand), and then about 500 cc. of concentrated sulphuric acid is poured upon the mercury and from 25 to 50 grams of mercurous sulphate is added. In the top of the separatory funnel is placed an ordinary funnel, the stem of which is drawn out to small diameter and turned upward. The mercury to be purified is poured into this latter funnel and flows slowly and in the form of a fine spray out of the end of the stem. It is freed from foreign metals that stand above it in the electromotive series by the action of the sulphuric acid and mercurous sulphate, and is thoroughly dried by passing through the concentrated acid, so that fairly pure and dry mercury may at any time be drawn off from the separatory funnel. In starting the process, impure mercury which may first have been put into the funnel should, of course, be drawn off and run through the purifier a second time. The mercury in the separatory funnel should never be drawn down until it is near the stopcock, for some sulphuric acid might be drawn off with it.

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[18] *J. Am. Chem. Soc.*, **31**, 933 (1909).
[19] *Am. Chem. J.*, **41**, 152 (1909).
[20] *Am. Chem. J.*, **46**, 594 (1911).
[21] Wolff and Walters, *Bureau of Standards, Sci. Papers* No. 67, 70, 71 (1907).
[22] *Ind. Eng. Chem.*, **9**, 600 (1917).

Purification of Mercury by Distillation.—This method should be the final step in the purification and it gives satisfactory results if the mercury is free from oxides, and if bumping of the liquid during distillation is avoided (see p. 112). If foreign oxides are present, they should first be removed by one of the methods already described.

Of the many forms of apparatus that have been suggested for the distillation of mercury, the modified form of Weinhold's still[23] shown in Fig. 60 is one of the simplest and most efficient for obtaining mercury of sufficient purity for gas analysis. All glass parts of the device are of pyrex glass. The mercury is boiled in the bulb *A* which has a diameter of about 7 cm. The neck of *A* is fused to the outside of the tube *G* just above *B*, and has a side arm *K* that is connected with the level-bulb *M* by a piece of "varnished" rubber tubing.[24] To the lower side of the bulb *B* is attached a tube of 5 mm. internal diameter, and 15 cm. long, and to this is fused the capillary tube *C* which has a bore of about one mm. diameter, and a length of about 800 mm. The lower end of *C* is bent upward and widened at *D*, and then is brought out over the middle of the box and turned downward at *E*.

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[23] Weinhold-Carl's *Rep.*, **9**, 68 (1873).

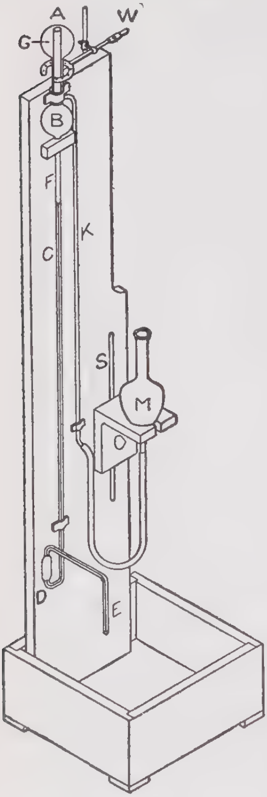

FIG. 60

To start the distillation, dry mercury that has been freed from oxides by treatment with nitric acid is poured into the level-bulb *M*, and the capillary tube *E* is connected with a mercury pump or with an efficient water suction-pump if a mercury pump is not available. *M* is then raised until the mercury rises in *A* nearly to the top of the tube *G*, and the pumping is continued until all the air possible has been drawn out of *B* through *C*. *M* is then slipped into its adjustable support, and this is set at such a height in the slot *S* by means of a set screw that the bulb *A* is about half filled with mercury. The ring burner *W* is now lighted and the mercury is carefully brought to boiling. The height of the level-bulb *M* is readjusted so that the bulb *A* stands half full of mercury. The vapor of the mercury passes from *A* down through *G* into *B*, and the condensed metal flows through the open end of the capillary *E* into a container placed below *E* to receive it.

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[24] See p. 100.

With this type of distillation apparatus Hulett states[25] that metals with appreciable vapor pressure, such as zinc, cadmium, etc., will distill over even when present in very small amounts. If, however, a small amount of air is bubbled through the mercury during distillation, he states[26] that all oxidizable metals may be removed by a single distillation, and non-oxidizable metals such as silver, gold and platinum, by two or three distillations. He has designed two forms of distillation apparatus working on this principle. Duschak and Spencer[27] have modified the apparatus (Fig. 60) to allow the admission of air during distillation. Booth and Jones[28] have constructed a similar still out of glass-enamelled metal, but do not state the purity of the distilled mercury.

[25] Hulett and Minchin, *Phys. Rev.*, **21**, 388 (1905).
[26] Hulett, *Phys. Rev.*, **33**, 312 (1911).
[27] *J. Phys. Chem.*, **21**, 311 (1917).
[28] *Ind. Eng. Chem.*, **19**, 104 (1927).

CHAPTER XI

ABSORPTION APPARATUS FOR USE WITH LARGE VOLUMES OF GAS

Gases that are very soluble in water or that are present in only small amount in a mixture of gases are best determined by passing the gas mixture through suitable absorption apparatus to remove these constituents, and then ascertaining the quantity of the absorbed gas by gravimetric or volumetric methods. The total volume of the gas mixture that is passed through the absorption apparatus is measured by a suitable device, such as an experimental gas meter. The meter is placed before the absorption apparatus if the gas that is to be determined is not appreciably soluble in water. Otherwise it is placed after the absorbent.

This method of analysis is particularly well adapted to the determination of minute amounts of a gas in a gas mixture for the reason that the large size of the sample that may here be employed renders the results very accurate if the absorbed constituent is correctly determined. To illustrate how slight is the effect, upon the final result, of a considerable error in the measurement of the sample, let us suppose that, in the determination of carbon dioxide in air, a sample of ten liters has been passed through the apparatus and the titration shows four cc. of carbon dioxide, or 0.04 per cent. If a mistake of 100 cc. were made in the measurement of the sample, which would be a very large experimental error, the result calculated for 10100 cc. would be 0.0396 per cent carbon dioxide, and for 9900 cc., 0.0404 per cent. To obtain the same accuracy by the volumetric analysis of a sample of air measuring 100 cc. the readings would have to be correct to the hundredth of a cubic centimeter.

Gas washing-bottles or absorption apparatus may be classified[1] as: (1) those with the sole object of purifying the gas, with no further use of the absorbing liquid; (2) those for determining the constituent by gravimetric analysis or by titration; and (3) those for determining the constituent by the increase in weight of the apparatus caused by the absorption. Friedrichs has pointed out the chief requirements which gas absorption apparatus should fulfill, and has grouped all the known forms into the three following types: (1) ordinary, (2) those with bulbs or pieces of glass in the inlet tube (see pp. 234 and 389), and (3) those of the spiral design.

The absorption of the gas depends upon: (1) the velocity of the gas stream, (2) the concentration of the gas mixture, (3) the concentration of the absorbing medium, (4) the size of the gas bubbles, and (5) the duration of the action of the absorbing medium. Thus to effect the complete absorption of a gas by a liquid, it is necessary that the gas be broken up into fine bubbles before or while passing through the absorbent, or that it remain in contact with the liquid for a considerable length of time. The former procedure, being more rapid, is usually to be preferred. He investigated[2] twenty-seven kinds of gas washing-bottles of the above three types and found that only the washing-bottles of the spiral type insure complete absorption when only one is used.

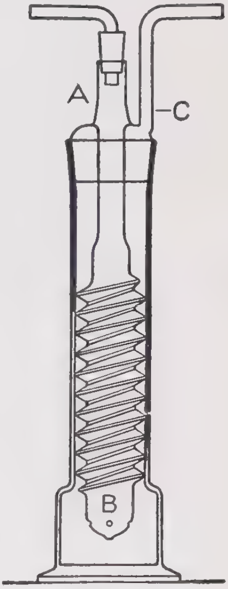

FIG. 61

A form of the spiral gas washing-bottle that has been thoroughly tested in the Cornell laboratory and found to be very efficient is shown in Fig. 61. It is a slight modification[3] of the spiral gas washing-bottle designed by Friedrichs.[4]

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[1] Friedrichs, *Z. angew. Chem.*, **32**, 252 (1919).
[2] Friedrichs, *loc. cit.*
[3] Dennis and O'Brien, *Ind. Eng. Chem.*, **4**, 834 (1912).
[4] *Z. anal. Chem.*, **50**, 175 (1911).

In preparing the bottle for use, the stopper with the attached inner cylinder is removed, and the absorbing liquid is introduced into the outer cylinder in such amount that when the inner cylinder is replaced the liquid will stand at the height of the lowest spiral. The gas enters the bottle at *A* and passes into the absorbing liquid through small openings in the bottom of the inner cylinder. It cannot escape directly upward, but must pass around the spirals, which it does in the form of a procession of gas bubbles that push ahead of them small amounts of the absorbing liquid. The contact between the gas and the absorbent is intimate and of considerable duration, and the consequent absorption is very complete. This form of the bottle was particularly designed for quantitative work. Upon removal of the small rubber stopper that is inserted in *A* the absorbing liquid in the bottle can easily be removed, and the bottle be thoroughly rinsed out. If, however, the na-

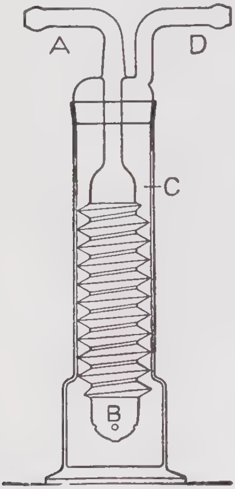

Fig. 62

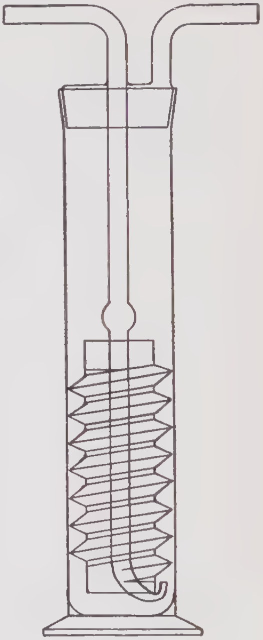

Fig. 63

ture of the work is such as to render undesirable the use of a rubber stopper in *A*, the tube *A* may be made somewhat longer and bent at a right angle (Fig. 62), which will permit of a glass-to-glass connection of the apparatus.

In order to increase the circulation of the absorbing liquid and to prevent any trapping of the gas on the inside of the spiral, Milligan[5] has modified the Friedrichs wash-bottle as shown in Fig. 63. The gas carries the liquid up between the outside of the spiral and the inside of the bottle, the liquid returning between the inside of the spiral and the inlet tube. The opening at the top of the spiral is elliptical, so that when gas bubbles tend to lift the spiral, it is brought to rest against the little bulb at the center of the inlet tube.

If it is desired merely to remove a gas from a gas mixture, but not afterward to determine its amount, the apparatus devised by Winkler[6] may be used. In this Winkler absorption apparatus, however, the gas that rises through the cylinder comes in contact with only such portion of the absorbent as adheres to the surface of the pumicestone. Moreover if a large amount of gas is being removed by the absorbent, the liquid must frequently be driven up into the pumicestone by blowing into a side tube. A modification of the apparatus that gives more efficient absorption and automatically renews the absorbent is shown in Fig. 64. A Friedrichs spiral absorption tube fits by a ground joint into one neck of a Wolff bottle that contains the solution of the

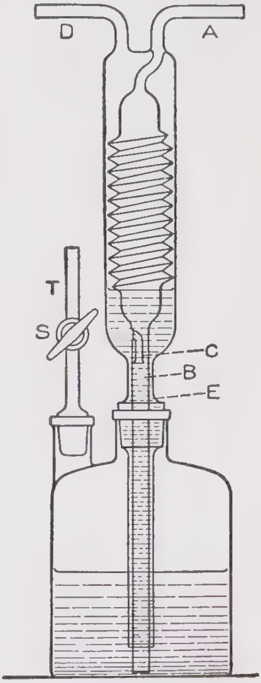

FIG. 64

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[5] *J. Phys. Chem.*, **28**, 554 (1924); *Ind. Eng. Chem.*, **16**, 889 (1924).
[6] Dennis, *Gas Analysis* (1913), p. 125.

absorbent. Into the other neck of the Wolff bottle is inserted by means of a ground joint a short glass tube *T* carrying the stopcock *S*. Some of the reagent is driven up into the absorbing cylinder by opening *S* and blowing into *T*, whereupon *S* is closed. The gas mixture enters through the tube *A* and, passing downward in the inside of the spiral, it enters the tube *B* and passes upward through the open lower end of the short tube *C*. It then rises around the spiral carrying some of the liquid with it, and the non-absorbed gases escape at *D*. As the gas bubbles rise through the short tube *C* they draw up fresh absorbent through the tube *B* and the absorbent that has been in contact with the gas flows downward through the tube *E* into the Wolff bottle below. In this manner constant circulation of the absorbing liquid is attained and the apparatus requires no further attention after once it has been set in action.

CHAPTER XII

THE COMBUSTION OF GASES

Most gases may quantitatively be removed by absorbents, and for this reason the combustion method is chiefly employed for the determination of only hydrogen, methane and its homologues, and at times carbon monoxide. Under certain conditions, however, it may be advisable to determine the amounts of other constituents of a gas mixture by direct combustion even although these gases may be absorbable by suitable reagents. It is not always possible to ascertain from the results of a single combustion the percentage of each constituent in the gas mixture. De Voldere and de Smet[1] have developed certain fundamental laws which show the possibilities and limitations of the combustion method, and the following condensation and revision of their original article was prepared by Dr. R. P. Anderson.

According to de Voldere and de Smet the gases that may accurately be determined by combustion analysis are divisible into three classes:

I. Hydrocarbons.

$C_nH_{2n} + 2k$, where $k = 1$, 0, —1, —2, or —3. It is convenient to include under this head CO, CO_2, O_2, and H_2 because the combustion equations of these gases are of the same type as those of the hydrocarbons, as is evident if the proper values are given to n and k. For example,

if $n = 0$ and $k = 1$, $C_nH_{2n} + 2k$ becomes C_0H_2, equivalent to H_2
if $n = 1$ and $k = -2$, $C_nH_{2n} + 2k$ becomes C_1H_{-2}, equivalent to CO
if $n = 0$ and $k = -2$, $C_nH_{2n} + 2k$ becomes C_0H_{-4}, equivalent to O_2
if $n = 1$ and $k = -3$, $C_nH_{2n} + 2k$ becomes C_1H_{-4}, equivalent to CO_2

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[1] *Z. anal. Chem.,* **49**, 661–688 (1910).

II. Gases containing carbon, hydrogen, and oxygen.

Formic aldehyde, CH_2O; methyl ether, $(CH_3)_2O$; methyl ethyl ether, $(CH_3C_2H_5)O$; ethyl ether, $(C_2H_5)_2O$; acetaldehyde, C_2H_4O.

III. Gases containing nitrogen.

Nitrogen, N_2; nitrous oxide, N_2O; ammonia, NH_3; hydrogen cyanide, HCN.

Other combustible gases such as the hydrides of the fifth and sixth groups of the Mendeléeff periodic arrangement, halogen and sulphur hydrocarbon substitution products, and gaseous compounds of nitrogen other than those given above, yield combustion products that are not suited to gas-volumetric determination. The following discussion is confined to combinations of gases of the first class, finally amplified to include nitrogen or one of the other nitrogen-containing gases. For details concerning the combustion of gas mixtures containing members of all three of the above classes, the reader is referred to the original article.

In the combustion of a hydrocarbon four factors are determinable. These factors together with the symbols that will here be used to represent them are as follows:

V, the total volume of gas to be burned;

O_2, the volume of oxygen necessary for the complete combustion of the gas;

CO_2, the volume of carbon dioxide that is formed in the combustion;

T. C., the total contraction in volume that results from the combustion.

This total contraction is equal to the sum of the volume of the hydrocarbon and of that of the oxygen used, less the volume of carbon dioxide that is formed. The water that is produced in the combustion condenses to the liquid state.

$$\mathrm{T.\,C.} = V + O_2 - CO_2. \qquad (1)$$

The complete combustion of a hydrocarbon, $C_nH_{2n} + 2k$, may be expressed by the equation,

$$C_nH_{2n} + 2k + \frac{3n + k}{2} O_2 = nCO_2 + (n + k)H_2O.$$

In this case—

$$\mathbf{O_2} = \frac{3n + k}{2} \mathbf{V} \tag{2}$$

$$\mathbf{CO_2} = n\mathbf{V} \tag{3}$$

$$\mathbf{T.\ C.} = \frac{2 + n + k}{2} \mathbf{V} \tag{4}$$

The following table gives the values of $\mathbf{O_2}$, $\mathbf{CO_2}$, and **T. C.** per unit volume of hydrocarbons of the various groups.

TABLE VII

k	GROUP	O_2	CO_2	T. C.	EXAMPLES
1	$C_nH_{2n} + 2k$	$\frac{3n + 1}{2}$	n	$\frac{n + 3}{2}$	CH_4, C_2H_6, C_3H_8, H_2
0	C_nH_{2n}	$\frac{3n}{2}$	n	$\frac{n + 2}{2}$	C_2H_4
− 1	$C_nH_{2n - 2}$	$\frac{3n - 1}{2}$	n	$\frac{n + 1}{2}$	C_2H_2
− 2	$C_nH_{2n - 4}$	$\frac{3n - 2}{2}$	n	$\frac{n}{2}$	CO, O_2
− 3	$C_nH_{2n - 6}$	$\frac{3n - 3}{2}$	n	$\frac{n - 1}{2}$	CO_2

The four factors, **V**, $\mathbf{O_2}$, $\mathbf{CO_2}$, and **T. C.** can also be determined in the combustion of any mixture of hydrocarbons, and by means of equations expressing the relationships between these four factors and the unknown volumes of the gases that are present, the volumes can, in certain cases, be computed. A study of these equations shows that the number of gases that can be determined depends upon the nature of the gas mixture. The different possibilities are discussed under the following cases:

FIRST CASE. **It is possible, by means of one complete combustion, to determine the percentage composition of a gas mixture that contains not more than two hydrocarbons of the same group, provided the formula of each constituent is known.**

If a gas mixture were to contain several gases of one group, say Group I, the equations between the knowns and unknowns would be derived as follows:

Let x, y, z, . . . = volumes of the gases present
and n, n′, n″ . . . = indices of gases x, y, z . . .

Then (from Table I),

$$\mathbf{V} = x + y + z + \cdots \tag{5}$$

$$\mathbf{O_2} = \frac{3n + 1}{2}x + \frac{3n' + 1}{2}y + \frac{3n'' + 1}{2}z + \cdots \tag{6}$$

$$\mathbf{CO_2} = nx + n'y + n''z + \cdots \tag{7}$$

$$\mathbf{T.\,C.} = \frac{n + 3}{2}x + \frac{n' + 3}{2}y + \frac{n'' + 3}{2}z + \cdots \tag{8}$$

These four equations are not independent as can be shown by the following eliminations:

$$2O_2 - V - 3CO_2 = 0 (2\text{xEqn. } 6 - \text{Eqn. } 5 - 3\text{xEqn. } 7) \tag{9}$$

$$2T.\,C. - CO_2 - 3V = 0 (2\text{xEqn. } 8 - \text{Eqn. } 7 - 3\text{xEqn. } 5) \tag{10}$$

Equations 9 and 10 represent the peculiar relations that exist between the four determinable factors when the gases belong to the same group, and this relation is such that the determination of any two of these factors enables one to compute the other two; hence there are in reality only two independent equations, and *not more than two* gases of this group could be determined by a single combustion. Similar relations hold true for the other groups and the analogous equations are given in the following table:

TABLE VIII

GROUP	EQUATIONS	
C_nH_{2n+2}	$V = \frac{2\ T.C. - CO_2}{3}$	$V = \frac{3\ CO_2 - 2\ O_2}{-1}$
C_nH_{2n}	$V = \frac{2\ T.C. - CO_2}{2}$	$V = \frac{3\ CO_2 - 2\ O_2}{0}$
		or $3\ CO_2 = 2\ O_2$
C_nH_{2n-2}	$V = 2\ T.C. - CO_2$	$V = 3\ CO_2 - 2\ O_2$
C_nH_{2n-4}	$V = \frac{2\ T.C. - CO_2}{0}$	$V = \frac{3\ CO_2 - 2\ O_2}{2}$
	or $2\ T.C. = CO_2$	
C_nH_{2n-6}	$V = \frac{2\ T.C. - CO_2}{-1}$	$V = \frac{3\ CO_2 - 2\ O_2}{3}$

It is apparent also that the formulas of the individual gases are necessary, since otherwise two new unknowns, n and n′, would be introduced and the number of unknowns would exceed the number of independent equations.

A gas mixture that rather frequently occurs in technical practice is one containing hydrogen, methane and ethane. These three gases are hydrocarbons of the same group under the classification that is here employed, and since they belong to the same group, they cannot be determined by a single combustion. *If, in the analysis of this gas mixture, the results of the combustion are computed for hydrogen and methane alone, the volume of methane will be too large by twice the volume of the ethane that is actually present, and the volume of hydrogen will be too small by a volume equal to that of the ethane that is present, entirely independent of the relative percentages of each.*

The following calculation will make this clear:

Let $\mathbf{H_2}$, $\mathbf{CH_4}$ and $\mathbf{C_2H_6}$ represent the volumes of hydrogen, methane, and ethane in a mixture of these three gases.

Then, giving the proper values to n, n′, and n″ in equations 7 and 8,

$$\text{T. C.} = \frac{3}{2}\mathrm{H_2} + 2\mathrm{CH_4} + \frac{5}{2}\mathrm{C_2H_6} \tag{11}$$

and

$$\mathrm{CO_2} = \mathrm{CH_4} + 2\mathrm{C_2H_6} \tag{12}$$

Now, let x and y represent the amounts of hydrogen and methane obtained when the computation is based upon these two gases.

Then

$$\text{T. C.} = \frac{3}{2}x + 2y \tag{13}$$

and

$$\mathrm{CO_2} = y \tag{14}$$

$$\frac{3}{2}x + 2y = \frac{3}{2}\mathrm{H_2} + 2\mathrm{CH_4} + \frac{5}{2}\mathrm{C_2H_6}(\text{Eqn. 11} - \text{Eqn. 13}) \tag{15}$$

$$y = \mathrm{CH_4} + 2\mathrm{C_2H_6}(\text{Eqn. 12} - \text{Eqn. 14}) \tag{16}$$

$$x = \mathrm{H_2} - \mathrm{C_2H_6}\left(\frac{2}{3}[\text{Eqn. 15} - 2\text{xEqn. 16}]\right) \tag{17}$$

For example, if a gas mixture contains equal volumes of hydrogen, methane, and ethane, and the combustion data are computed for hydrogen and methane alone, the result would indicate that the gas mixture contains only methane (see Equations 16 and 17).

In the analysis of such gas mixtures as coal gas, producer gas, or water gas, the residue after the removal of the absorbable constituents is frequently assumed to consist of hydrogen, methane and nitrogen, and a calculation of the combustion results is based upon this assumption. It is clear from what has been stated above that this assumption may lead to errors of considerable magnitude in the percentages of hydrogen and methane if ethane is present. The percentage of nitrogen, however, is not affected, since the sum of the percentages of hydrogen and methane apparently present is equal to the sum of the percentages of hydrogen, methane and ethane actually present.

Second Case. **It is possible, by means of one complete combustion, to determine the percentage composition of a gas mixture that contains not more than three hydrocarbons, two of them of the same group, provided the formula of each constituent is known.**

If a gas mixture of this type were to contain two gases of Group I and one gas of each of the remaining groups, the equations would be derived as follows:

Let x, y, z, . . . = volumes of the two gases of Group I and the gases from the other groups respectively, and n, n′, n″, . . . = indices of gases x, y, z, etc.

Then,

$$\mathbf{V} = x + y + z + \cdots \tag{18}$$

$$\mathbf{O_2} = \frac{3n+1}{2}x + \frac{3n'+1}{2}y + \frac{3n''}{2}z + \cdots \tag{19}$$

$$\mathbf{CO_2} = nx + n'y + n''z + \cdots \tag{20}$$

$$\mathbf{T.\ C.} = \frac{n+3}{2}x + \frac{n'+3}{2}y + \frac{n''+2}{2}z + \cdots \tag{21}$$

But inasmuch as

$$\mathbf{V} + \mathbf{O_2} = \mathbf{CO_2} + \mathbf{T.\ C.} \text{ (see Equation 1)} \cdots \tag{22}$$

holds true for the combustion of any mixture of hydrocarbons, it is clear that if three of the four factors, **V**, $\mathbf{O_2}$, $\mathbf{CO_2}$, and **T. C.**, are known, the fourth may be computed. From this it follows that there are really only three independent equations, and for this reason more than three hydrocarbons, two of them of the same group, cannot be determined by a single combustion. Moreover, as was shown under First Case, the formula of each gas must be known.

Third Case. **It is usually possible by means of one complete combustion to determine the percentage composition**

of a gas mixture that contains not more than three hydrocarbons, all of them of different groups, provided the formula of each constituent is known.

If a gas mixture of this type were to contain one gas from each group, the equations would be derived as follows:

Let x, y, z, . . . = volumes of gases of 1st, 2d, 3d . . . groups,

and n, n′, n″ . . . = indices of gases, x, y, z . . . etc.

Then

$$V = x + y + z + \cdots \tag{23}$$

$$O_2 = \frac{3n+1}{2}x + \frac{3n'}{2}y + \frac{3n''-1}{2}z + \cdots \tag{24}$$

$$CO_2 = nx + n'y + n''z + \cdots \tag{25}$$

$$T.\,C. = \frac{n+3}{2}x + \frac{n'+2}{2}y + \frac{n''+1}{2}z + \cdots \tag{26}$$

For the same reasons as those given under Second Case, *not more than three* hydrocarbons belonging to different groups can be determined, and the formula of each must be known. But in mixtures that would be classed under the Third Case there may exist a peculiar relation between the indices of the various gases that will render the equations indeterminate. For example, if a gas mixture contains one gas from each of the following groups, C_nC_{2n+2}, C_nH_{2n-4}, and C_nH_{2n-6}, then

$$V = x + y + z \tag{27}$$

$$2O_2 = (3n+1)x + (3n'-2)y + (3n''-3)z \tag{28}$$

$$2T.\,C. = (n+3)x + n'y + (n''-1)z \tag{29}$$

$$CO_2 = nx + n'y + n''z \tag{30}$$

Solving for x (or y or z),

$(4n' - 3n'' - n)x$ = some expression in terms of **V**, $\mathbf{O_2}$, **T. C.**, and $\mathbf{CO_2}$. (31)

When the relation between n, n′ and n″ is such that

$4n' - 3n'' - n = 0$, or $n' = \frac{3n'' + n}{4}$, the equation is indeterminate. This is true when $n = n' = n'' = 1$, as for example when the gas mixture contains methane, carbon monoxide, and carbon dioxide.

Since the gases classified under the Third Case may belong to any one of five groups (see p. 125) there are ten possible combinations under this case.

If the five groups are represented by A, B, C, D, E, and the indices of the three gases in the mixture are represented by n, n′ and n″ in the order of the groups, then the determinants and the indeterminate examples among the gases in Table VII may be tabulated as follows:

TABLE IX

COMBINATION	DETERMINANT	INDETERMINATE EXAMPLES
A B C	$n' = \frac{n'' + n}{2}$	C_2H_6, C_2H_4, C_2H_2
B C D		
C D E		
A C E		C_3H_8, C_2H_2, CO_2
A B D	$n' = \frac{n'' + 2n}{3}$	C_3H_8, C_2H_4, O_2
B C E		
A C D	$n' = \frac{2n'' + n}{3}$	
B D E		
A B E	$n' = \frac{n'' + 3n}{4}$	
A D E	$n' = \frac{3n'' + n}{4}$	CH_4, CO, CO_2

FOURTH CASE. **When a gas mixture contains hydrocarbons that belong to not more than two groups, the percentage of each group in the mixture may be determined by**

means of one complete combustion if the general formula of each group is known.

Let **V** be a mixture of two groups, of volumes X and Y to be determined, each a mixture of several gases x_1, x_2, x_3, . . . and y_1, y_2, y_3, ...

Also let n_1, n_2, n_3, . . . and n'_1, n'_2, n'_3, . . . be the indices of the gases, and k and k′ the constants of the two groups.

Then $$\mathbf{V} = x_1 + x_2 + x_3 \cdots + y_1 + y_2 + y_3 \cdots \qquad (32)$$

$$\mathbf{CO_2} = n_1x_1 + n_2x_2 + n_3x_3 \cdots + n'_1y_1 + n'_2y_2 + n'_3y_3 \cdots \qquad (33)$$

$$\mathbf{2T.\ C.} = (n_1 + k + 2)x_1 + (n_2 + k + 2)x_2 \cdots + (n'_1 + k' + 2)y_1 + (n'_2 + k' + 2)y_2 \cdots \qquad (34)$$

$$\mathbf{2O_2} = (3n_1 + k)x_1 + (3n_2 + k)x_2 \cdots + (3n'_1 + k')y_1 + 3n'_2 + k')y_2 \cdots \qquad (35)$$

Then (Eqn. 34 − 2 Eqn. 32 − Eqn. 33)

$$\mathbf{2T.\ C.} - \mathbf{2V} - \mathbf{CO_2} = k(x_1 + x_2 + x_3 \cdots) + k'(y_1 + y_2 + y_3 \cdots)\cdots \qquad (36)$$

(Simplifying Eqn. 36)

$$\mathbf{2T.\ C.} - \mathbf{2V} - \mathbf{CO_2} = kX + k'Y \qquad (37)$$

(Simplifying Eqn. 32) ⋯

$$\mathbf{V} = X + Y \qquad (38)$$

From equations 37 and 38 the values X and Y can be determined when k and k′ are known.

GASEOUS HYDROCARBONS AND NITROGEN

If nitrogen is present with the gaseous hydrocarbons, the total contraction of combustion (see p. 124) is equal to the sum of the volume of the mixture and the volume of the necessary oxygen, less the sum of the volume of carbon dioxide formed and the volume of nitrogen present, or

$$\mathbf{T.\ C.} = \mathbf{V} + \mathbf{O_2} - \mathbf{CO_2} - \mathbf{N_2} \qquad (39)$$

where $\mathbf{N_2}$ represents the volume of nitrogen in the gas mixture. The introduction of the unknown, $\mathbf{N}_2$ in the preceding equation renders the four equations between the four determinable factors and the unknowns independent when the hydrocarbons are not all of the same group (Second and Third Cases) and gives three independent equations when the hydrocarbons are all of the same group (First Case). Thus it is seen that the presence of nitrogen in a mixture that is otherwise composed entirely of hydrocarbons increases the number of independent equations by one and thereby provides for its own determination. In general, the determinability of any hydrocarbon mixture is not affected by the presence of an unknown amount of nitrogen.

This also holds true if the nitrogen be replaced by ammonia, or nitrous oxide, or hydrogen cyanide, if the necessary changes are made in the expressions involving $\mathbf{O}_2$, $\mathbf{CO}_2$, and **T. C.**

Summary

1. More than *three* gaseous hydrocarbons cannot be determined by one complete combustion.
2. Two gaseous hydrocarbons of known composition and of the same group can always be determined by one complete combustion.
3. Three gaseous hydrocarbons of known composition, two of which belong to the same group, can always be determined by one complete combustion.
4. Three gaseous hydrocarbons of known composition, but which belong to different groups, can usually be determined by one complete combustion (note exceptions).
5. In a mixture of hydrocarbons of two groups, the percentage of each group can be determined by one complete combustion.
6. Any of the mixtures that have been mentioned above is still determinable even if an unknown quantity of nitrogen is present.

INDENTIFICATION OF GASEOUS HYDROCARBONS [2]

To identify a gaseous hydrocarbon or to determine the relative amounts of carbon and hydrogen in a mixture of hydrocarbons, it is necessary only to burn a measured volume of the gas with oxygen and to determine the total contraction and the carbon dioxide formed. From these data the calculation may be made as follows:

$$C_nH_m + \left(n + \frac{m}{4}\right) O_2 = nCO_2 + \frac{m}{2} H_2O$$

and if **V** = the volume of the gas sample

$$VC_nH_m + V\left(n + \frac{m}{4}\right) O_2 = VnCO_2 + V\frac{m}{2} H_2O$$

Since the total contraction, **T. C.** = **V** + **O$_2$** − **CO$_2$** (see p. 124), then, in the present case,

$$\mathbf{T.\ C.} = \mathbf{V} + \mathbf{V}n + \mathbf{V}\frac{m}{4} - \mathbf{V}n \qquad \text{or}$$

$$\mathbf{T.\ C.} = \mathbf{V} + \mathbf{V}\frac{m}{4} \qquad \text{and}$$

$$m = \frac{4(\mathbf{T.\ C.} - \mathbf{V})}{\mathbf{V}}$$

Since $\mathbf{CO_2} = \mathbf{V}n,$

$$n = \frac{\mathbf{CO_2}}{\mathbf{V}}.$$

MOLECULAR VOLUMES OF GASES

In the determination of inflammable gases by combustion over mercury, it should be borne in mind, that, if great accuracy is desired, correction must be introduced for the variation of the actual molecular volumes of certain gases from the molecular volumes calculated for these gases on the basis of Avogadro's hypothesis. The gram-molecular volume of a gas, that is, the volume, under standard conditions, occupied by the molecular weight of a gas in grams, is in all cases nearly 22.412 liters, the value for an ideal gas. Yet the gases with which we chiefly have to do in combustion analysis show slight variations from this mean, and in one case, that of carbon dioxide, the difference is considerable.

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[2] See also Burgess and Wheeler, *J. Chem. Soc.*, **105**, 133 (1914).

Wohl has pointed out[3] that when gases that contain carbon are burned, an error too great to be disregarded in exact work will result if correction is not introduced for the low molecular volume of carbon dioxide. The molecular volume of carbon dioxide is 99.4 per cent that of carbon monoxide. Consequently when carbon monoxide is burned, the gas volume changes are accurately represented, not by the usual equation,

$$\begin{gathered} 2\ CO + O_2 = 2\ CO_2 \\ 2 \text{ vol.} + 1 \text{ vol.} = 2 \text{ vol.} \end{gathered}$$

but by the following,

$$\begin{gathered} 2\ CO + O_2 = 2\ CO_2 \\ 2 \text{ vol.} + 1 \text{ vol.} = 2 \times .994 = 1.988 \text{ vol.} \end{gathered}$$

If then the carbon monoxide is calculated directly from the contraction, the result will be 1.2 per cent of the true volume of carbon monoxide too high. Similarly if the carbon monoxide is determined by absorption of the carbon dioxide formed, the result will be 0.6 per cent of the true volume of carbon monoxide too low.

Wohl, however, assumed that these expressions which he derived, showing the exact proportions of gases entering into reaction with each other, could be applied in all cases. These equations apply only when the carbon dioxide produced is 95 to 100 per cent of all the gases remaining after combustion. Haber[4] showed by means of van der Waals' equation that the deviation is due to the fact that, at 0° and 760 mm., carbon dioxide is not a perfect gas, and that the deviation has nothing to do with Avogadro's theory. Therefore, if the partial pressure of the gas is below one atmosphere, the gas will behave more nearly like an ideal gas. Consequently, if such a small quantity of combustible gas is taken for the analysis that the carbon dioxide produced by combustion does not exceed 30 per cent of the total quantity of gas measured, the use of corrected equations for calculating the percentages of combustible gases from the experimental data is unnecessary. Burrell and Siebert[5] have pointed out that in the analysis of some mixtures rich in combustible gas, so small a proportion of the original gas has to be used in order to keep the partial pressure of the carbon dioxide produced below 30 per cent, that a large error is introduced by a small error of manipulation being magnified many times when the calculation to a percentage basis is made. Thus an error in reading of 0.1 cc. may introduce an error of 2 per cent.

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[3] *Ber.*, **37**, 429 (1904).

[4] Haber, *Thermodynamics of Technical Gas Reactions* (1906), pp. 306, 308.

TABLE X

Molecular Volumes of Gases

Gas	M	Specific Gravity (Air = 1)		
		Theoretical	Observed	Molecular Volume
H_2	2.016	0.06965	0.06952	1.002
O_2	32.00	1.1055	1.1055	1.000
N_2	28.02	0.9680	0.9672	1.001
CO	28.00	0.9673	0.9672	1.000
CO_2	44.00	1.5201	1.5291	0.994
CH_4	16.03	0.5538	0.5545	0.999
C_2H_6	30.05	1.0381	1.0494	0.990
C_3H_8	44.06	—	—	0.986*
C_2H_4	28.03	0.9683	0.9852	0.983
C_2H_2	26.02	0.8989	0.9056	0.992
N_2O	44.02	1.5208	1.5298	0.994

* Burrell, Siebert, and Robertson, *Bureau of Mines, Tech. Paper* No. 104 (1915), p. 14.

[5] *Bureau of Mines, Tech. Paper* No. 54 (1913).

Table X[6] gives the molecular volumes of some of the gases from specific gravity determinations at 0° C. and 760 mm. pressure.

In many cases the partial pressure of the gases can be kept low and the use of the corrections may thus be avoided, while at the same time the volume of the sample will be large enough to eliminate appreciable increase of the experimental error. However, for mixtures where the carbon gases constitute almost all of the sample, it is better to use such a quantity of the sample that the oxygen added will be only a few cc. in excess of that theoretically required and to apply the corrected equations. For further details of the corrections to be applied, the reader is referred to the paper of Burrell and Siebert.[7]

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[6] Landolt and Börnstein, *Physikalisch-Chemische Tabellen* (1912), p. 148.

[7] Burrell and Siebert, *loc. cit.*

CHAPTER XIII

THE DETERMINATION OF GASES BY COMBUSTION

ANALYSIS BY EXPLOSION

The Explosion Pipette for Technical Gas Analysis (Fig. 65).—This consists of the thick-walled explosion-bulb *A* and the level-bulb *B*, which are joined together by a piece of "varnished" rubber tubing *T*. The explosion bulb is supported by Plaster of Paris *P* as shown in the figure. At *C* two fine platinum wires are fused into the explosion pipette, the ends of the wires being about 2 mm. apart. At *D* is a glass stopcock, and the pipette terminates in the capillary *K*, whose end is closed by a short piece of rubber tubing *S* and a stout pinchcock.

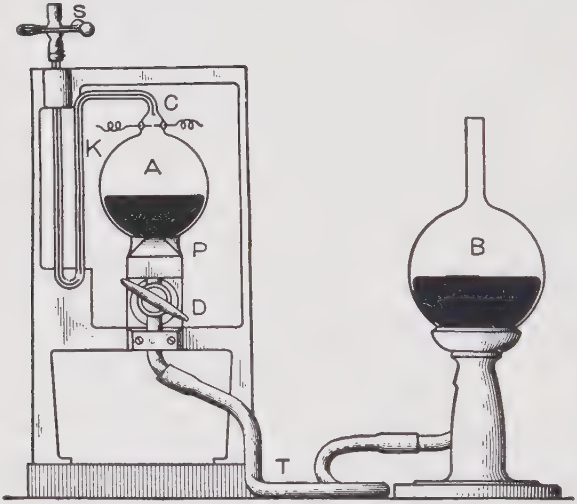

Fig. 65

The gas mixture that is to be exploded is introduced into the bulb *A*, the gas is brought approximately to atmospheric pressure, and the glass stopcock *D* is closed. The rubber tube *S* is next closed by the pinchcock, and a piece of glass rod is slipped into the end of the rubber tube. The pipette is then vigorously shaken to insure full mixture of the gases, the terminals at *C* are connected with the poles of an induction coil, a screen of plate glass is placed in front of the pipette and the current is turned on. The stopcock *D* is now opened at once, and the gas in the pipette is transferred without delay to the burette, and is measured at once if the burette is filled with mercury, or after one minute if the burette contains water.

In general, the pipettes and burettes for technical gas analysis are filled with aqueous solutions, but the explosion pipette is filled with mercury. By using mercury as confining liquid during the explosion it is possible afterward to determine the carbon dioxide formed in the combustion. If the explosion is made over water, a subsequent measuring of the carbon dioxide formed is inadmissible, because the pressure in the pipette is so high during the explosion that considerable quantities of carbon dioxide are absorbed by the water. By exploding over mercury very satisfactory results are obtained, even if the carbon dioxide is afterward measured in a burette that contains water as the confining liquid.

If the explosion is too violent it is possible that some oxides of nitrogen may be formed, if nitrogen is present. On the other hand, if the combustion in the pipette proceeds too slowly, the oxidation of the gases is probably not complete. The closing of the capillary of the explosion pipette in the manner above described furnishes not only a sort of safety-valve for the release of pressure if the explosion is too violent, but also affords means of judging the energy of the explosion. If the explosion has the proper intensity, there will be a quick jerk of the rubber tube at the moment of explosion, but both pinchcock and glass plug will remain in place. With too violent an explosion, the pinchcock is forced open, and the glass plug is driven out of the rubber tube. If the combustion is not sufficiently vigorous, no movement of the rubber tube is seen. From these statements it is apparent that the suggestion [1] to modify the Hempel explosion pipette by placing a glass stopcock at the upper end of the capillary *K* not merely exposes the operator to the danger of accident through the bursting of the pipette, but also deprives him of a means of judging the intensity of the explosion.

It has been proposed [2] to modify the explosion pipette by the introduction of one of the wires through the bottom of the pipette to prevent the electric current from traveling around the walls of the pipette when they are wet instead of sparking across the gap.

Proportion of Gases in Analysis by Explosion.—Bunsen found that—

100 vol. of air with 13.5 oxyhydrogen gas would not burn.

								Vol. of Air Remaining
100	air	burned	with	26.26	oxyhydrogen	gas,	left	100.02
100	“	“	“	34.66	“	“	“	100.15
100	“	“	“	43.72	“	“	“	100.07
100	“	“	“	51.12	“	“	“	99.98
100	“	“	“	64.31	“	“	“	99.90
100	“	“	“	78.76	“	“	“	99.43
100	“	“	“	97.84	“	“	“	96.92
100	“	“	“	226.04	“	“	“	88.56

These results led Bunsen to recommend that in the determination of hydrogen by explosion not less than 26 volumes nor more than 64 volumes of combustible gas be used to 100 volumes of incombustible gas. It should, however, be borne in mind that the above proportions refer only to the explosion of mixtures of hydrogen and oxygen. With combustible gases other than hydrogen quite different ratios should be used.

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[1] Pfeiffer, *Chem. Ztg.*, **28**, 686 (1904); Tiddy, *Gas World*, **79**, 187 (1923).

[2] Gill, *J. Am. Chem. Soc.* **17**, 771 (1895); White and Campbell, *ibid.*, **27**, 734 (1905).

This is evidenced by the results of Teclu[3] who finds that mixtures of hydrogen, methane, acetylene and illuminating gas are explosive only when the amount of the combustible gas lies between the following percentage volumes:

Hydrogen,	about	10	to	63	per	cent
Methane,	"	3.5	"	8	"	"
Acetylene,	"	2.5	"	80	"	"
Illuminating gas,	"	5	"	25	"	"

Formation of Oxides of Nitrogen.—It was long supposed[4] that if the explosion of gas mixtures was made under the conditions that Bunsen laid down, the formation of oxides of nitrogen would always be avoided. Experimental evidence[5] seemed to show that when nitrogen is present, oxides of nitrogen are produced in varying amounts, and that the quantity might at times be so appreciable as to introduce a considerable error in the results of analysis.

Jones and Parker[6] have found that the production of oxides of nitrogen is due to the flame temperature developed by the gas mixture when exploded rather than to the sparking across the electrodes. If oxygen is used, appreciable quantities of oxides of nitrogen are formed because of the increase in the flame temperature. If, however, air is used as the oxygen supply, no oxides of nitrogen are produced.

A further source of possible error in the determination of hydrogen by explosion has been pointed out by Misteli[7] who states that small amounts of hydrogen escape combustion.

Induction Coil.—For producing the spark for the explosion a small induction coil[8] will be found adequate. The current for operating this coil may be obtained from either dry or wet cells or from a storage battery or from a dynamo with sufficient resistance in the circuit.

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[3] *J. prakt. Chem.*, **75**, 212 (1907); see also Burrell, *Ind. Eng. Chem.*, **5**, 181 (1913).

[4] Hempel, *Gasometrische Methoden* (1900), p. 113.

[5] White, *J. Am. Chem. Soc.*, **23**, 476 (1901).

[6] *Ind. Eng. Chem.*, **13**, 1154 (1921).

[7] *J. Gasbel.*, **48**, 802 (1905).

[8] The small induction coil used in the Ford automobile has been found to be very satisfactory for this purpose.

Preparation of Pure Hydrogen and Oxy-Hydrogen Gas.—If a gas mixture contains so small an amount or combustible gas that it will not explode when mixed with oxygen or air, pure hydrogen or oxy-hydrogen gas is added to the mixture. For the preparation of hydrogen gas for this purpose, the Hempel hydrogen pipette may be used.[9] In this device the hydrogen is obtained by the action of dilute sulphuric acid on zinc.

The purity of the hydrogen evolved in this pipette will, of course, depend upon the purity of the acid and zinc that are employed. White[10] recommends the use of potassium hydroxide or aluminum to obtain the hydrogen free from the small amounts of hydrocarbons usually present in the gas obtained by the action of an acid on a metal. Edwards[11] has described an apparatus for the generation of pure hydrogen by the action of sulphuric acid on zinc, and Sveda[12] has suggested a modified form of the apparatus of Bayerle and Tamele in which the hydrogen is generated by the action of dilute (1:1) hydrochloric acid upon a concentrated amalgam of zinc and mercury in contact with a platinized platinum electrode. The hydrogen is then passed through a 50 per cent solution of potassium hydroxide and finally over solid, re-fused potassium hydroxide.

Oxy-hydrogen gas may conveniently be generated in the apparatus of Hempel[13] in which the gas is formed by the electrolysis of a dilute solution of sulphuric acid between platinum electrodes.

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[9] Dennis, *Gas Analysis* (1913), p. 144.

[10] *J. Am. Chem. Soc.*, **23**, 478 (1901).

[11] *Ind. Eng. Chem.*, **11**, 961 (1919).

[12] *Chem. News*, **130**, 3 (1925).

[13] Hempel, *Gasanalytische Methoden* (1903), p. 108.

ANALYSIS BY COMBUSTION

Combustion with an Electrically Heated Platinum Spiral

The Combustion Pipette.—Coquillion[14] was the first to propose the use of a glowing platinum spiral in the determination of such gases as marsh-gas and hydrogen. Winkler improved the form of the apparatus and used a Hempel pipette for solid and liquid reagents. While adhering in the main to the Winkler arrangement, Dennis and Hopkins[15] modified the apparatus so that mercury may be used as the confining liquid. This permits of a much more accurate determination of carbon monoxide or hydrocarbons than is possible over water. The cylindrical portion of a Hempel simple pipette for solid and liquid reagents, *A*, Fig. 66, is fastened to the stand in the usual manner, except that the bulb is supported by a small block of Plaster of Paris, *P*. In the neck of the pipette is inserted a two-hole rubber stopper *S*

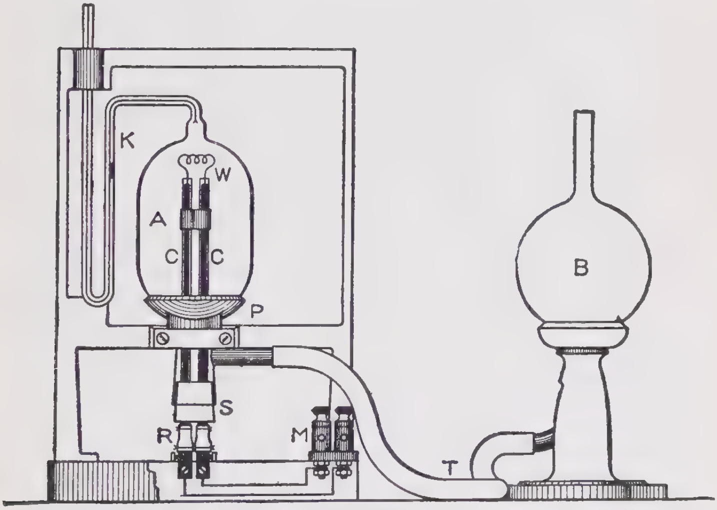

Fig. 66

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[14] *Compt. rend.*, **83**, 394 (1876); **84**, 458, 1503 (1877).

[15] *J. Am. Chem. Soc.*, **21**, 398 (1899).

through the openings of which glass tubes *CC* pass from below the stopper to within about 20 mm. of the top of the pipette. Inside each glass tube is a stout iron wire 2.5 mm. in diameter which reaches nearly to the top of the glass tube and projects about 10 mm. below the lower end. To the lower end of each iron wire there is attached a small binding post and the connection between the glass tube and the binding post is made air-tight by slipping over the ends of each a short piece of rubber tubing *R* which is then securely wired in place. Small iron screws are threaded into openings in the upper ends of the two iron wires, and serve to hold in place the ends of the platinum spiral *W*. A strip of iron about one cm. wide is bent in the form of an S around the two glass tubes about midway up in the bulb of the pipette for the purpose of holding the tubes more rigidly in position. A piece of double-bored capillary tubing may be used instead of the two glass tubes for the iron leads. The platinum spiral that connects the upper ends of the two iron wires is made of platinum wire ¼ mm. in diameter which is bent in a coil about 2 mm. in diameter and contains from 20 to 30 turns. The ends of the platinum wire are fastened under the two small screws in the upper ends of the iron wires. The two binding posts that are fastened to the lower ends of the iron wires are connected to two larger binding posts *M* fastened into a plate of hard rubber that is itself attached to the base of the iron frame. The combustion pipette is usually filled with mercury which is introduced through a small funnel inserted in the tube of the level-bulb *B*. After the pipette has been filled with the mercury, the air that may be trapped by the mercury in the glass tubes surrounding the iron wires is removed by closing the capillary tube of the pipette with a piece of rubber tube and pinchcock and attaching a water suction pump to the tube of the level-bulb.

When the pipette is constructed and is filled with mercury in the manner above described, the iron wires passing through the glass tubes do not come into contact with the gas mixture in the pipette at any point, for when a gas is passed into the pipette the glass tubes remain filled with mercury which covers the ends of the iron wires. This makes it entirely unnecessary to use heavy platinum wires in the place of the iron wires as has been recommended by Porter and Ovitz.[16]

Manipulation of the Combustion Pipette.—In carrying out a combustion with this pipette, a measured amount of oxygen (about 100 cc.) is passed into it from a gas burette and the gas to be burned is then measured off in the burette. Ordinarily the total unabsorbable residue from a gas sample of about 100 cc. is used in the combustion, but the volume of the sample taken should be of such size that after combustion an excess of oxygen remains in the pipette. The gas burette *H* is connected with the combustion pipette by the usual bent capillary tube, and the wires from the source of current are fastened to the binding posts on the frame of the pipette (Fig. 67). A small rheostat[17] *R* is introduced into the circuit to permit of ready control of the current flowing through the platinum spiral and thus to enable the operator to keep the spiral at dull redness throughout the combustion. The current for heating the spiral may be that from a storage battery or from a dynamo, or more conveniently the alternating current of a lighting circuit. If the alternating current is employed, the connections may be made as shown in the figure. A plug carrying two wires is screwed into an ordinary lamp socket; one of the wires is connected with the rheostat and with a bank of lamps *L* connected in parallel. The further terminal of the lamps is connected with one of the binding posts *M* on the pipette, and the other binding post is connected directly to the current supply. The coarser adjustment of the current is made by means of the lamps and the finer adjustment by means of the rheostat.

Different gases show great differences in heat conductivity, and if adjustment of the current were not easily possible the spiral might be raised to so high a temperature during the process as to melt the platinum wire. For example, when hydrogen is burned in the pipette by first introducing that

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[16] *Bureau of Mines, Bulletin 1* (1910), p. 24.

[17] A Cutler-Hammer 16 ohm, 6.4 amp., 40 volt field rheostat is very satisfactory for this purpose.

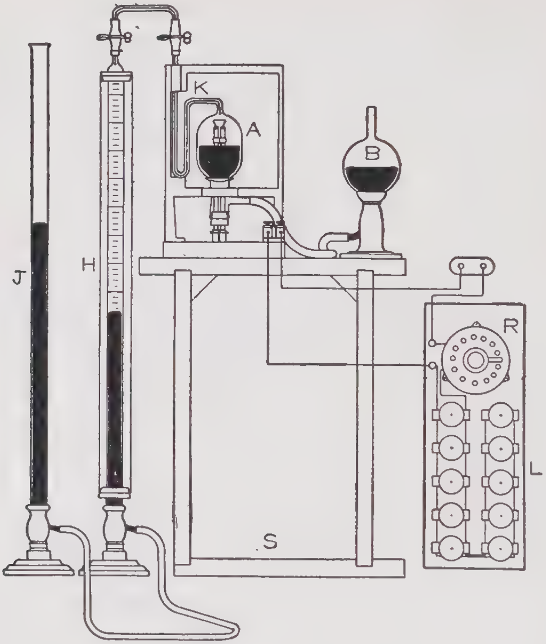

Fig. 67

gas and then admitting a mixture of air and oxygen, a current that will at the beginning heat the spiral only to redness in the atmosphere of hydrogen will bring the platinum wire to a bright yellow glow and will at times melt it in the mixture of nitrogen and oxygen that remains after the hydrogen has been burned. After the combustible gas has been introduced, the platinum spiral is kept at dull redness for 60 seconds. The current is then turned off, the pipette is allowed to cool, and the gas residue is passed back into the burette and measured. Air or a mixture of oxygen and air may be used in the pipette in place of pure oxygen. If the combustible gas contains acetylene or its homologues it should be run into the pipette very slowly and under a pressure that is only very slightly above that of the prevailing atmospheric pressure. If this precaution is not taken, dissociation is liable to occur when the gas comes in contact with the hot spiral, and the separated carbon would of course then escape combustion.

In most cases the process may be reversed and the combustible gas be first introduced into the pipette, and oxygen or air or a mixture of the two then passed in from the burette. This manipulation is, however, not suited to the combustion of acetylene because the hot spiral causes decomposition of this gas with the deposition of solid carbon.

The chief merits of this method of combustion are:

(1) The use of a large volume of combustible gas with consequent increase in the accuracy of the results;

(2) The avoidance of explosion by the *gradual* addition of oxygen to the combustible gas or of the combustible gas to oxygen;

(3) The avoidance of the formation of measurable amounts of the oxides of nitrogen in the combustion of gas mixtures that contain nitrogen.

Weaver and Ledig[18] have suggested a modified form of this pipette in which the platinum spiral leads are introduced through the sides, thus eliminating the necessity of a stopper at the bottom. Kaleta[19] has suggested a modification so that the gas is impinged directly on the hot spiral causing it to burn smoothly with a visible flame. He has used this same type of pipette for the determination of carbon monoxide[20] in blast-furnace gas.

Rischbieth[21] has described a method whereby this type of combustion pipette may be used for the fractional combustion of hydrogen and methane in mixtures with air, and Gilbert[22] has devised a manostat for supporting the levelling-bulb *B* to

[18] *Ind. Eng. Chem.*, **12**, 368 (1920).

[19] *Chem. Ztg.*, **45**, 651 (1921).

[20] *Chem. Ztg.*, **46**, 430 (1922).

[21] *Chem. Ztg.*, **46**, 784 (1922).

[22] *Ind. Eng. Chem.*, **6**, 585 (1914).

insure constant pressure in the combustion by maintaining a constant level of the mercury.

Formation of Oxides of Nitrogen in Combustion Pipette.—Some years ago White stated[23] that oxides of nitrogen are formed when hydrogen is burned with oxygen and air in this pipette, and he based this statement upon the fact that he obtained a reaction for nitrites with Griess's reagent after heating air alone in the combustion pipette, and further that there was contraction in volume when the products of the combustion of hydrogen with oxygen and air were passed into a pipette containing potassium hydroxide.

The experiments of White were carefully repeated[24] and extended at the request of one of the authors, and it was found that no measurable amount of oxides of nitrogen is formed when the conditions given by Dennis and Hopkins[25] are followed, and the platinum spiral is heated only to dull redness during the combustion and is kept at dull redness for no longer than sixty seconds after the gases have been introduced into the pipette. When the temperature of the spiral was raised beyond a dull red heat, the amount of the oxides of nitrogen that was formed increased with rise of temperature, but the total amount of the product even after heating the air for five minutes with the spiral at a bright yellow was not measurable in a Hempel burette over mercury.

In the combustion of hydrogen with a mixture of oxygen and air, Rhodes found that when the spiral is properly heated, the amount of oxides of nitrogen that was produced is slightly higher than when air alone is heated, but that the volume of this product was in no case large enough to permit of its volumetric measurement when 100 cc. of hydrogen was burned. To ascertain whether an appreciable error would result in the combustion of hydrogen with a mixture of air and oxygen when the spiral was highly heated, 100 cc. of hydrogen was introduced into the pipette, the spiral was heated to bright yellow, and 100 cc. of a mixture of equal volumes of air and oxygen was slowly passed in. The colorimetric determination of the amount of nitrite formed when the products were passed into the sodium hydroxide showed that even under these unusual conditions, the volume of the oxides of nitrogen that was formed was less than 0.01 of a cc., an error that is entirely negligible in technical gas analysis when working with a gas sample of 100 cc. In the analysis of gas mixtures that commonly occur in technical practice, the error would be very much less than that above cited because of the lower percentage of hydrogen.

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[23] *J. Am. Chem. Soc.*, **23**, 476 (1901).

[24] Rhodes, Dennis' *Gas Analysis* (1913), p. 153.

[25] *J. Am. Chem. Soc.*, **21**, 398 (1899).

Hempel[26] also contended that oxides of nitrogen are formed when the combustion is continued long enough to ensure the oxidation of all the methane. He further stated that oxidation of the mercury caused high results. However, Jones and Parker[27] thoroughly investigated this method and found that not more than 0.003 cc. of oxides of nitrogen is formed when the time of burning is not more than three minutes and the wire is not heated beyond a bright yellow. They also found that the purity of the platinum wire has no effect on the quantity of oxides of nitrogen produced. Therefore any error introduced by the production of oxides of nitrogen is within the experimental error of ordinary gas analysis.

This method of combustion is also the basis for the forms of apparatus that have been designed[28] for the detection of combustible gases in air.

Combustion with a Platinum Capillary Tube.—In order to determine combustible gases without the employment of an electric current, Drehschmidt[29] used a platinum capillary tube, filled with fine platinum wire, which was heated to the requisite temperature by a gas flame. This method is unsatisfactory because when heated with an ordinary Bunsen burner the combustion of methane is not complete and the tubes begin to leak after having been in use only a comparatively short time, which constitutes a serious drawback when the high cost of the tube and the difficulty of repairing it in the laboratory are taken into consideration.

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[26] *Z. angew. Chem.*, **25**, 1841 (1912).

[27] *Ind. Eng. Chem.*, **13**, 1154 (1921).

[28] Beckmann and Steglich, *Chem. Ztg.*, **39**, 3 (1915); Burrell, *Ind. Eng. Chem.*, **8**, 365 (1916); Milligan, *Bureau of Mines, Tech. Paper* No. 357 (1925).

[29] *Ber.*, **21**, 3242 (1888); see also Ott, *J. Gasbel.*, **63**, 198, 213, 246, 267 (1920); Steuer, *Chem. Ztg.*, **49**, 901 (1925).

Hempel [30] improved this apparatus by inserting in a transparent quartz capillary tube a platinum spiral which almost fills the tube. The quartz tube is fastened between two glass capillary tubes by rubber tubing. The platinum spiral can be heated either by a small blast flame or by means of an electric current. Mathers and Lee [31] suggest the use of a quartz tube filled with pieces of scrap platinum. Levy [32] has modified the tube by sealing the platinum wire into the quartz capillary by means of molybdenum leads. This form has no rubber connections but is expensive and it is difficult to replace the wire in case it is broken or burned out. White [33] also modified the method of inserting the platinum wire, but he still used a rubber connection between the quartz and glass tubes. Weaver and Ledig [34] have modified the tube to permit the easy replacement of the platinum wire and to eliminate rubber connections. This tube may be made of pyrex glass, which is more economical, but it must be surrounded by a water jacket to prevent the softening of the tube when the wire is heated hot enough to burn methane. If the mixture of gas and air is passed slowly over the hot platinum spiral, there is no danger of an explosion [35] and the temperature will not rise high enough to cause the formation of oxides of nitrogen.

It is not safe, however, to dilute a large sample of gas with pure oxygen, because the capillary tube cannot be relied upon to prevent an explosion in this case.

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[30] *Z. angew. Chem.*, **25**, 1841 (1912).
[31] *Chem. Eng.*, **17**, 159 (1913).
[32] *J. Soc. Chem. Ind.*, **31**, 1153 (1912).
[33] White, *Gas and Fuel Analysis* (1920), p. 51.
[34] *Ind. Eng. Chem.*, **12**, 368 (1920).
[35] Hempel, *loc. cit.*

In carrying out a combustion with this apparatus the measured sample of gas to be burned is passed over into the simple gas pipette, and an amount of air that is sufficient to burn the combustible constituents of the gas mixture is measured off in the gas burette. This is passed into the pipette and the pinchcock at the top of the pipette is closed.

The capillary tube is then placed in position between the burette and the pipette, the burette being of course filled to the top with the confining liquid. The combustion tube is heated to bright redness by means of a burner or the electric current, the pinchcocks on the pipette and burette are then opened and the gas is slowly drawn over into the burette. Two passages of the gas through the capillary suffice for complete combustion. The capillary tube is then allowed to cool and the residual gas is drawn into the burette and measured. The simple pipette is now replaced by a pipette containing potassium hydroxide, and the carbon dioxide is removed [36] and the gas residue is again measured. If hydrogen and methane are being simultaneously determined, results of only approximate accuracy are obtainable when water is used as the confining liquid in the burette and pipette. In such case it is therefore preferable to use a pipette with level-bulb (see Fig. 49) and to employ mercury as the confining liquid in both the pipette and the burette.

Fractional Combustion with Platinum or Palladium Asbestos.—The first method of fractional combustion was proposed by Henry [37] who found that he could remove hydrogen and carbon monoxide from the mixture of these two gases with methane and nitrogen by passing the gases over platinum sponge heated to 177°. Coquillion later discovered [38] that hydrogen and methane, when mixed with air, could be burned by passing the gases over a spiral of metallic palladium heated to bright redness by an electric current.

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[36] Unless a small bore capillary tube is used, a correction must be made for the carbon dioxide remaining in the quartz tube after the combustion.

[37] *Annals of Philosophy*, **25**, 428 (1825).

[38] *Compt. rend.*, **83**, 799 (1876); **84**, 1503 (1877); **85**, 1106 (1878).

1878 Bunte described [39] a method for the combustion of hydrogen in which the mixture of the gas with air or oxygen is passed over palladium that is heated externally to the desired temperature by means of a small flame. It was afterward found that if the temperature to which the metallic palladium is heated is kept below a certain point, methane does not burn and that consequently the determination of hydrogen when admixed with methane may be effected in this manner.

The use of palladium asbestos for the combustion of hydrogen was first suggested by Winkler.[40] According to him methane is not burnt at all when passed over palladium asbestos heated by a free flame; even with a considerable excess of easily combustible gases present, there is only a slight trace, if any, of methane burnt. Palladium sponge [41] and platinum asbestos [42] have also been suggested as contact substances for the combustion of hydrogen. Hempel [43] states that methane when passed over palladium asbestos at 100° does not burn, but that above 200° a portion of the methane is burned along with hydrogen.

Phillips [44] found that the oxidation of methane by palladium asbestos occurs at 404° to 414° C. and that a variation in the proportion of combustible gas and air does not seem to affect the temperature of combustion.

To ascertain the temperature at which methane, when mixed with air, will be oxidized upon passage over a catalytic agent Richardt [45] passed the mixture over palladium wire that was placed in a capillary tube which was heated from the outside by a small flame. He employed palladium wire instead of palladium asbestos because the compact metal, having high heat conductivity, rendered it possible to avoid local superheating. He found that methane was oxidized to some extent at a temperature but slightly above 450° and that it rapidly burned at temperatures above 700°. From these measurements it is evident that if the catalytic substance is heated to a dull red glow that is visible in daylight, which according to Richardt corresponds to a temperature from 750° to 800°, combustion of some of the methane will undoubtedly result.

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[39] *Ber.*, **11**, 1123 (1878); *J. Gasbel.*, **21**, 263 (1878).
[40] *Anleit. z. chem. Unters. der Industrie-Gase*, Part 2, p. 258.
[41] Hempel, *Ber.*, **12**, 1006 (1879).
[42] Kopfer, *ibid.*, **9**, 1377 (1876).
[43] Hempel, *Gasanalytische Methoden* (1900), p. 162.
[44] *Am. Chem. J.*, **16**, 163 (1894).
[45] *Z. anorg. Chem.*, **38**, 65 (1904); *J. Gasbel.*, **47**, 566, 590 (1904).

Moreover, he has pointed out that finely divided contact substances such as palladium asbestos, platinum asbestos or palladium sponge are poor heat-conductors, and for this reason the heat developed by the combustion of the gases within the tube may locally raise the catalyst to a temperature at which methane will burn, even when the external heating of the tube is very carefully regulated. The observation of Winkler[46] that even when the glass capillary tube containing palladium asbestos is very carefully heated by a small gas flame "the end of the asbestos thread against which the entering current of gas impinges is heated to a bright glow, and that this glow is frequently again seen when the gas sample is passed back into the burette," is one that is familiar to all who have used this method of fractional combustion.

Results confirmatory of the statements of Richardt were later obtained by Denham[47] who found that the temperature of combustion of practically pure methane and oxygen when the gas mixture is passed through a tube containing palladium asbestos lies between 514° and 546°.

Brunck maintains[48] that the results obtained in the fractional combustion of hydrogen by means of palladium asbestos are accurate even when the asbestos thread visibly glows during the passage of the gas mixture, but even his own confirmatory analyses show that with slight elevation of the temperature of the capillary tube, some methane is oxidized. If the palladium asbestos glows during the passage of the gas its temperature is undoubtedly considerably above 500°. With this fact in mind it is difficult to reconcile the statements of Brunck with the experimental results of Nesmjelow[49] which appear to demonstrate that when a mixture of hydrogen, methane and air is passed through a capillary tube that contains palladium asbestos, an appreciable amount of methane is oxidized at 150°. It is certainly the case that when the fractional combustion of hydrogen by means of palladium asbestos is carried out in the manner prescribed in almost all of the various descriptions of the method, the temperature of 150° will be greatly exceeded, particularly when a porous catalyst is employed.

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[46] Winkler, *Lehrbuch der technischen Gasanalyse* (1901), p. 168.
[47] *J. Soc. Chem. Ind.*, **24**, 1202 (1905).
[48] *Z. angew. Chem.*, **16**, 695 (1903).

In a review[50] of this method Hempel found that hydrogen may be determined with accuracy in the presence of methane and ethane if the palladium asbestos does not glow during the analysis, and if the temperature of the capillary itself does not rise appreciably above 400°. He stated that this may be accomplished by heating the capillary in a certain manner, which he describes, and by passing the gas mixture very slowly through the tube, and that if these directions are followed *with the greatest care* the method gives agreeing results. These statements by Hempel serve to accentuate the uncertainty inherent in the fractional combustion of hydrogen by means of a catalytic substance that is heated with a free flame, and they render it evident that slight variations in the procedure may easily give rise to errors of considerable magnitude.

Nesmjelow[51] gives the following directions for the preparation of palladium asbestos.

Dissolve three grams of sodium palladious chloride in as small an amount of water as possible, add three cc. of a cold, saturated solution of sodium formate, and then sodium carbonate to strong alkaline reaction. Place in the solution one gram of long-fibered, soft asbestos which will absorb practically all of the liquid. Dry the fiber on the water-bath. Metallic palladium will hereupon separate evenly on the asbestos in a black, finely divided form:

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[49] *Z. anal. Chem.,* **48**, 232 (1909).
[50] *Z. angew. Chem.,* **25**, 1841 (1912).
[51] *Loc. cit.*

$$Na_2PdCl_4 + HCOONa = 3NaCl + HCl + CO_2 + Pd.$$

After complete drying on the water-bath, the asbestos is softened with water, and then is placed in a funnel and washed with warm water until the adhering salts are removed. It is then dried and kept in stoppered glass bottles.

If it is desired to prepare this solution from metallic palladium, the metal is dissolved in aqua regia, the solution of the chloride is evaporated to dryness on a water-bath to remove the free acid, the residue is then dissolved in a small quantity of water and the solution is treated as above.

The asbestos may also be soaked in a concentrated solution of palladium chloride,[52] but in this case it must be heated to a dull red heat to decompose the chloride.

A few of the threads of palladium asbestos about one centimeter long are moistened and inserted in the middle of a capillary tube about 8 cm. long and 1 mm. bore. The asbestos is then dried on a water-bath, and the tube is bent into the usual form of a capillary connecting tube.

The tube containing the palladium asbestos is connected between the burette and a pipette, is then heated to the desired temperature, and the mixture of gas and air is passed slowly through it. If oxygen is used, there is danger that an explosion may result. The palladium asbestos must be kept dry as it is not active when moist.

Fractional Combustion of Hydrogen with Palladium Black (Hempel).[53]—The method is based upon the fact that if a mixture of hydrogen, methane and air, oxygen being present in excess, is passed over palladium black at a temperature not above 100°, hydrogen alone is burned.

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[52] Campbell and Hart, *Am. Chem. J.*, **18**, 294 (1896).

[53] *Ber.*, **12**, 1006 (1879); Hempel, *Gasanalytische Methoden* (1913), p. 163.

Finely divided palladium is prepared for use in this method by heating it to redness upon the lid of a platinum crucible and gradually removing it from the flame so that it will cool slowly. This covers the metal with a very thin layer of palladious oxide. About 0.5 gram of this palladium black is placed in a small U-shaped glass tube. This tube is connected by short pieces of rubber tubing with bent capillary tubes, one of which is joined to a gas burette while the other is connected with a simple gas pipette filled with water.

From 15 to 20 cc. of the mixture of hydrogen and methane is brought into a Hempel burette and accurately measured. There is then drawn into the burette such an amount of air as will insure the presence of more than enough oxygen to unite with the hydrogen in the gas mixture. The total volume of the gas is now measured. The right-hand capillary having been connected with a gas pipette filled with water, the left hand capillary is now joined to the burette containing the gas sample and air, and a beaker containing water of a temperature of from 60° to 80° is brought up under the U-shaped tube and set at such a height that the water stands just below the lower ends of the rubber connections. The gas mixture in the burette is now passed *very slowly* through the palladium tube into the pipette. With too rapid a passage of the gas mixture over the palladium black the heat developed by the combustion of hydrogen may raise the palladium to a temperature at which methane will begin to burn. With reasonable care, however, the temperature of the U-tube and of its contents may easily be kept below 100° and the combustion of methane entirely avoided. The gas mixture is passed backward and forward from burette to pipette until no further decrease in the volume of the gas is observed. The beaker of warm water is then removed and is replaced by a beaker filled with water of the temperature of the room. When the residual gas has in this manner been brought to room temperature, the diminution of the volume of the gas is read. The volume of hydrogen in the sample is equal to two-thirds of the contraction noted.

An objection that may, however, be urged against this method is that only a portion of the combustible residue is employed and consequently an experimental error in the combustion is multiplied several times when the result is calculated for the total residue.

Fractional Combustion of Hydrogen with Copper Oxide (Jäger.)—The use of copper oxide for the determination of gaseous hydrocarbons was proposed by Fresenius as long ago as 1864,[54] and the method was afterward further developed by Scheurer-Kestner,[55] Stöckmann,[56] and Campbell.[57]

Jäger was the first to propose the use of copper oxide in the *fractional* combustion[58] of hydrogen in the presence of methane, hydrogen being completely burned when passed over copper oxide[59] at a temperature of 250°, whereas methane is not oxidized at all under these conditions. Jäger places copper oxide in a hard glass tube 6 cm. in length and one cm. in external diameter. One end of the tube terminates in a straight capillary tube 3 cm. long. To the other end is fused a glass tube 4 cm. in length and 5 mm. internal diameter through which the fine granular copper oxide is introduced. This combustion tube is connected on one side to a gas burette and on the other to a Hempel simple gas pipette containing a solution of potassium hydroxide.

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[54] *Z. anal. Chem.*, **3**, 339 (1864).

[55] Scheurer-Kestner, *Bull. de la Societe industrielle de Mulhouse*, 1868; *Civilingenieur, N. F.*, XV, 123.

[56] Stöckmann, *Die Gase des Hochofens und der Siemens-Generatoren*, Ruhrort 1876, 6.

[57] *Am. Chem. J.*, **17**, 688 (1895).

[58] *J. Gasbel.*, **41**, 764 (1898).

[59] The oxygen for the combustion of hydrogen comes from the solid copper oxide which on reduction decreases in volume. Consequently the results obtained by measuring the contraction of the gas volume are somewhat too high. The error from this source is, however, so very small that it may be entirely disregarded. For example, in the determination of hydrogen, the correction would be 0.00047 cc. for each cubic centimeter of the gas.

In the fractional combustion of hydrogen in a mixture of that gas with methane and nitrogen the combustion tube is first heated to 250°, and the gas mixture is then slowly passed through it from the burette into the pipette. Jäger found that a double passage of the gas through the tube usually suffices for the complete combustion of the hydrogen, but the gas mixture is usually passed through the tube a third time to ascertain whether further diminution in volume takes place. Since the oxygen of the air that is originally contained in the combustion tube burns with the hydrogen, the contraction due to this source must be ascertained. Jäger does this once and for all by passing through the heated combustion tube a mixture of known volumes of hydrogen and nitrogen. The observed contraction less the contraction due to the hydrogen used gives the volume of the oxygen in the combustion tube.

The method is distinctly superior to the fractional combustion of hydrogen by palladium or palladium asbestos because—

1. No air or oxygen is added to the combustible gas, which makes it possible to pass the total gas residue through the tube with consequent gain in accuracy of the analytical results;
2. The temperature at which the hydrogen burns, 250° C., is so easily controlled and is so far below the temperature at which methane will be oxidzed as to render impossible the combustion of any of the methane;
3. The material and apparatus are inexpensive;
4. The copper oxide does not become poisoned as is apt to occur at times with some of the palladium preparations.

To avoid the necessity of determining the volume of oxygen in the combustion tube and of making correction for it, von Knorre[60] first fills the tube with nitrogen, this gas being passed into the combustion tube through a T-tube that is introduced between the combustion tube and the pipette. He obtains the necessary volume of nitrogen by passing air into a phosphorus pipette (page 181) and he states that the nitrogen residue from 100 cc. of air is amply sufficient to displace the oxygen in the combustion tube.

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[60] *Chem. Ztg.*, **33**, 717 (1909).

Jäger recommended that the methane in the gas residue be determined, after the fractional combustion of hydrogen, by raising the temperature of the combustion tube to bright redness, passing the mixture of methane and nitrogen through the tube and ascertaining the volume of methane by determining either the contraction or the volume of carbon dioxide formed in the combustion. Methane, however, is not easily burned by passage over hot copper oxide, and complete combustion of the gas is effected only by repeatedly passing it through the combustion tube. Moreover, since the tube itself must be kept at a bright red heat throughout the process, it frequently softens, and if a drop of water enters it, it instantly breaks. These difficulties in the determination of methane are avoided by von Knorre by substituting for the hard glass tube a tube of transparent quartz 15 cm. long, 5 mm. internal diameter and with a thickness of wall of from 0.5 to 0.75 mm.

Nemsjelow[61] determines the carbon monoxide and hydrogen simultaneously by burning over copper oxide at 250° in the presence of oxygen, the copper oxide acting as a catalyst. He found that silver oxide could also be used, although it is not as practical.

Ubbelohde and de Castro[62] use a quartz tube filled with copper oxide surrounded by an asbestos oven, which they heat to 270° for the combustion of the hydrogen, and then to bright redness (800° to 900°) to burn the methane and ethane. In the latter combustion they heat the quartz tube with a free flame and place a clay trough over the tube to bring the temperature to the highest point possible.

They had to renew their copper oxide after fifteen to twenty analyses, as it was found to have lost its reactivity. The hydrogen is determined from the contraction in volume, and the volume of carbon monoxide from the volume of carbon dioxide. These two are exactly equal only when the sample is diluted by nitrogen or other gases.

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[61] *Z. anal. Chem.*, **48**, 232 (1909).
[62] *J. Gasbel.*, **54**, 810 (1911).

Terres and Manguin[63] state that hydrogen burns at from 160° to 170° and is completely oxidized at 250° to 300°. Dry carbon monoxide alone begins to oxidize at 145°, and when moist at 100°, but this combustion is not complete even at 305°. With a mixture of approximately equal parts of carbon monoxide and hydrogen, however, the combustion is complete at 305°, which makes possible the determination of carbon monoxide in the presence of methane. They further state that even when hydrogen is mixed with acetylene and ethylene, the latter gases do not burn completely on account of the deposition of carbon on the copper oxide. Benzene resembles ethylene as regards completeness of combustion. Methane begins to burn at 305° and is completely oxidized at red heat, providing the gas mixture contains over 1.5 per cent of methane. The authors also point out that at red heat the dissociation of copper oxide might cause appreciable errors.

Taplay[64] employed a temperature of 270° for the combustion of hydrogen, and 850° for the paraffin hydrocarbons. Worrell[65] used a silica tube and copper oxide passing an 80-mesh sieve. He heated the tube to a temperature of 250° to 260° for the combustion of hydrogen and carbon monoxide, and to red heat for the burning of methane.

Wibant[66] states that if cerium oxide is mixed with the copper oxide, the combustion of both hydrogen and methane is more rapid.

Taylor[67] recommends a temperature of 275° for the combustion of hydrogen and carbon monoxide, the tube of copper oxide being heated by a small electric furnace. The methane is determined by burning it with oxygen in a combustion pipette. The exact temperature for combustion that can be used will depend upon the nature of the hydrocarbons present; with methane alone 300° is probably not too high, but at this temperature there is danger of oxidation of the higher homologues of methane. Taylor has shown that hydrogen and carbon monoxide may be burned not only in the presence of methane without danger of oxidation of the latter, but also in the presence of high concentrations of the higher paraffins. He states that the time necessary for the complete combustion of hydrogen and carbon monoxide seems to depend upon the nature of the gas mixture rather than upon the quantity present. He concludes that generally when the contraction due to the burning of the hydrogen has ceased, the carbon monoxide may be assumed to be completely oxidized, unless it is present in much larger percentage than the hydrogen, in which case the passage through the copper oxide should be continued some minutes longer.

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[63] *J. Gasbel.*, **58**, 8 (1915).

[64] *J. Gas Lighting*, **118**, 217, 285 (1912).

[65] *Met. Chem. Eng.*, **11**, 245 (1913).

[66] *Chem. Weekblad*, **11**, 498 (1914).

[67] *Ind. Eng. Chem.*, **6**, 845 (1914).

Burrell and Oberfell[68] use the same type of tube of copper oxide as that which Taylor employed, and burn the carbon monoxide and hydrogen at 275° to 300°. They have found that carbon monoxide burns readily in the presence of hydrogen but much more slowly when burned alone. A maximum of about fifteen minutes is required to burn carbon monoxide and hydrogen completely in various gas mixtures.

The effect of the dissociation of the copper oxide has been investigated by Ott.[69] On passing pure nitrogen over copper oxide at red heat, he finds that the volume of the gas is markedly increased. If the temperature is then lowered to a dull red, this increase disappears, due no doubt to recombination of the oxygen with the copper. He also finds that nitrogen prepared from air by means of phosphorus contains vapor of phosphorus, and that if this nitrogen is then passed over copper oxide, a contraction of 0.2 per cent occurs. For accurate work he therefore recommends the absorption of oxygen from air by pyrogallol. Further, Ott always observed during the combustion of pure methane or carbon monoxide a contraction of at least 0.5 per cent which he considers to be due to the inaccuracy of the method. This influence of the dissociation of the copper oxide in gasometric analyses was also investigated by Bunte and Wunsch[70] who confirmed the results of Ott.

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[68] *Ind. Eng. Chem.*, **8**, 228 (1916).
[69] *J. Gasbel.*, **62**, 89 (1919).

Wollers[71] states that combustion either with copper oxide or with a platinum catalyst is more accurate for the determination of hydrogen and methane by combustion than is the explosion method. Wein[72] determines both hydrogen and methane in mine gases by passing the gas over hot copper oxide, and Dodge[73] uses this method for the determination of traces of nitrogen in hydrogen.

Scherb[74] has also investigated the combustion with copper oxide in the presence of an excess of oxygen. Hydrogen appears to burn completely at 295°. The difference in density of copper and copper oxide causes a correction of 0.01 cc. for 20 to 60 cc. of hydrogen. Carbon monoxide burns just as quantitatively at red heat as when burned by means of glowing platinum. The absorption of carbon dioxide by copper oxide seems to introduce an uncertainty; it appears to take place at ordinary temperatures and to increase to a maximum, diminishing again at higher temperatures; but all of the absorbed carbon dioxide is not liberated. Also, the absorption is directly proportional to the partial pressure of carbon dioxide. The presence of carbon dioxide seems to retard the combustion, so that carbon monoxide can be burned completely only when the carbon dioxide is simultaneously absorbed by alkali. Methane does not burn at 295° but is completely oxidized at red heat. He further points out that in the separation of hydrogen and carbon monoxide from methane, the absorption of the resulting carbon dioxide by copper oxide causes uncertainties and the amount of hydrogen affects the imflammability of carbon monoxide. Both hydrogen and carbon monoxide can be separated from methane at 295° if the carbon dioxide formed is absorbed at once by an alkali. Methane cannot be separated completely from ethane, but hydrogen can be.

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[70] *Gas u. Wasserfach,* **66**, 481 (1923).
[71] *Stahl u. Eisen,* **42**, 1050 (1922).
[72] *Chem. Ztg.,* **45**, 610 (1921).
[73] *J. Amer. Chem. Soc.,* **45**, 1688 (1923).
[74] *Gas u. Wasserfach,* **67**, 391 (1924).

Sveda[75] finds that hydrogen and carbon monoxide are burned completely at 280° to 290° in a closed space by electrically heating a small porous crucible filled with copper oxide. He also states that the absorption of carbon dioxide by the copper oxide introduces an error.

The catalytic oxidation of these gases by copper oxide in the presence of oxygen has been the subject of much study,[76] as has also the preferential[77] catalytic combustion of the gases in mixtures.

The Jäger method (p. 157) is very satisfactory for the accurate determination of hydrogen, but the subsequent combustion of methane at a higher temperature in the same tube cannot unqualifiedly be recommended. If hard glass is used for the combustion tube, the tube must either be ordered from a glass blower, or the chemist who makes his own simple glass apparatus must purchase both small tubing and capillary tubing of hard glass for fusion to the ends of the combustion tube proper. The glass tube is also apt to break when heated or when water is carelessly allowed to enter it during the combustion. The quartz tube is more durable, but apparatus of transparent quartz is fragile and expensive. The chief objection, however, to this method of determining methane lies in the fact that prolonged heating of the combustion tube to a high temperature and repeated passage of the gas through it are necessary for the complete oxidation of the methane. Because of these considerations the authors deem it preferable to restrict the combustion with copper oxide to the fractional combustion of hydrogen, and to determine the residual methane by combustion with oxygen in the Dennis combustion pipette. Since the combustion tube need be heated only to 250° if hydrogen alone is to be burned, this modification of the procedure makes it possible to use a tube of soft glass which can easily be blown by the operator himself. The subsequent determination of methane by means of the combustion pipette is fully as accurate as the combustion with copper oxide and is much more rapid. The following arrangement and manipulation of apparatus have been found to give very satisfactory results.

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[75] *Chem. News,* **130**, 1 (1925).

[76] Joannis, *Compt. rend.,* **159**, 64 (1914); Hofmann, *Ber.,* **51**, 1334 (1918); Palmer, *Brit. Assoc. Adv. Sci. Rep.* (1923), p. 435; Jones and Taylor, *J. Phys. Chem.,* **27**, 623 (1923); Almquist and Bray, *J. Amer. Chem. Soc.,* **45**, 2305 (1923).

[77] Bancroft, *Trans. Am. Electrochem. Soc.,* **32**, 465 (1917); Rideal, *J. Chem. Soc.,* **115**, 993 (1919); Rideal and Taylor, *Analyst,* **44**, 89 (1919); Lamb, Scalione, and Edgar, *J. Am. Chem. Soc.,* **44**, 738 (1922); Schuftan, *Z. angew. Chem.,* **39**, 276 (1926).

The combustion tube (Fig. 68) of pyrex glass consists of the piece of glass tubing *H*, 7 cm. long, 12 mm. external diameter, and one mm. thickness of wall; to one end of this tube is fused a piece of pyrex glass tubing 6 cm. long and 7 mm. external diameter; to the other end is fused a piece of pyrex capillary tubing of the dimensions used in the Hempel pipettes, namely, 6 mm. external diameter and one mm. internal diameter, which is then bent at a right angle as shown in the figure. *H* is filled through the wide end with granular copper oxide which is held in place by a loose plug of ignited asbestos. Inasmuch as the temperature of the copper oxide during the combustion should be kept nearly constant at 270°, the combustion tube is not heated with a free flame, but is placed either in a small air bath or a small electric heating furnace.

Ubbelohde and de Castro employ an oven made of sheet iron and lined with asbestos, and fitted with two perforated iron plates for the even distribution of the heat. A device that is simpler and fully as satisfactory may be constructed in the laboratory from ordinary asbestos board. A piece of asbestos board 9 cm. wide, 30 cm. long and 6 mm. thick is creased at points about 7.5 cm. apart, bent into a four-sided form and the ends connected by shaving one down to a sharp edge, splitting the other, inserting the narrow edge in the split end and then thoroughly wetting the asbestos and pressing it together. The two opposite sides of this box are notched to a depth of about 4.5 cm. and the small combustion tube rests in these notches. The box, which is open at the bottom, rests upon a piece of sheet iron that is supported on an iron ring, *M*. An asbestos top, with sides 6 cm. high, is made from asbestos board in the same manner, and opposite sides of the top

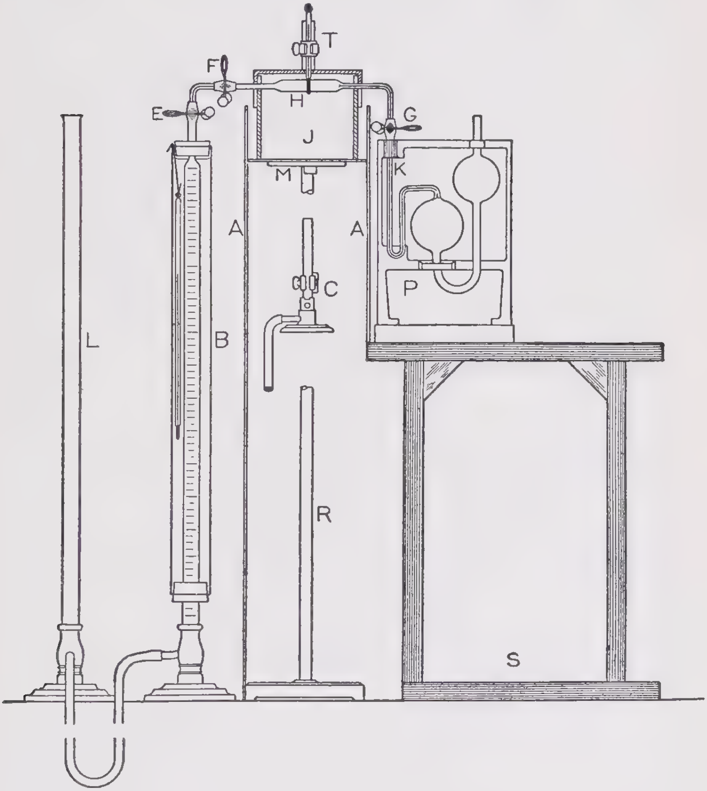

FIG. 68

are notched so that the top will set down over the box and completely close it except where the combustion tube passes through. A small opening in the top made with a cork borer serves for the introduction of the thermometer *T* which is placed in such position that its bulb rests against the side of the combustion tube. The air bath is heated by a single Bunsen burner, *C*. A flame about 6 cm. high suffices to keep the interior of the box and the combustion tube at a temperature of 270°. Although the little asbestos oven is not heated higher than the comparatively low temperature of 270° throughout the determination, it is advisable for the protection of the burette and the pipette to place strips of asbestos board, *AA*, about 15 cm. wide, between the pipette and the oven on the one side and the oven and the burette on the other.

The tube of copper oxide may also be heated very satisfactorily by a small electric furnace. This may be constructed by covering a quartz or alundum tube of about 20 mm. internal diameter and 13 cm. long, with a thin sheet of asbestos paper. Some nichrome wire of suitable size and length is wrapped around this to act as a heating coil. The tube is placed in the center of a soft glass tube about 45 mm. diameter and 12 cm. long, and the intervening space is packed with asbestos cement. The outside of the glass tube should then be covered with asbestos paper. The tube of copper oxide is held in the center of the furnace by a packing of asbestos at the end, or by corks with an opening to insert a thermometer with its bulb resting against the side of the combustion tube. To heat the tube, the heating unit is connected to a 110 volt A. C. or D. C. current in series with a suitable rheostat or lamp bank.

The tube for copper oxide and the electric furnace described by Taylor[78] are very suitable for this purpose.

In making a determination of hydrogen with this apparatus the combustion tube is placed in position in the heating apparatus, and its left-hand end, Fig. 68, is connected with a water-jacketed Hempel burette that contains water[79] as the confining liquid and that has previously been filled with nitrogen from a phosphorus pipette.[80]

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[78] *Ind. Eng. Chem.*, **6**, 845 (1914).

The pinchcock *E* at the top of the burette is opened and the nitrogen is passed through the combustion tube into the outer air. This washes out the air in the combustion tube, and frees it practically completely from all oxygen. The pinchcock *E* of the burette is closed and a simple gas pipette filled with water up to the top of the rubber connecting tube at *G* is at once joined to the combustion tube.

The rubber tube on the other end of the combustion tube is now closed by the pinchcock *F*, the burette is disconnected from the bent capillary tube and about 100 cc. of the gas mixture under examination, which should of course previously have been freed from all gases except hydrogen, nitrogen and members of the paraffin series, is drawn into the burette and measured. While this is being done the heating of the combustion tube is begun and the pinchcock *F* is opened for

[79] Mercury may of course be used as the confining liquid, and a burette with correction tube and manometer may be employed if great accuracy is desired. In technical practice, however, results that are correct to within one-tenth of one per cent are usually sufficiently accurate, and inasmuch as the manipulation of the apparatus is more simple and more rapid when water is used as the confining liquid instead of mercury, the method here described for the determination, over water, of not only hydrogen but of methane as well, has been worked out for the convenience of the general analyst. If methane is the only hydrocarbon that is present with the hydrogen, the two gases may more rapidly be determined by the simultaneous combustion of both with the combustion pipette, but in such case mercury must be used as the confining liquid in both burette and pipette. Furthermore, if two members of the paraffin group (*e.g.*, methane and ethane) are present in the gas residue after the hydrogen has been removed by fractional combustion with copper oxide, the two paraffins can be determined in the combustion pipette only when mercury is used as the confining liquid. In gas analysis, as in any other line of analytical work, it should constantly be borne in mind that the refinements of a method should be in accord with the accuracy that is desired. In the present instance, if results that are correct to within about one-tenth of one per cent meet the needs of the case, it would involve useless consumption of time to employ a very accurate gas burette and to measure the gases over mercury. On the other hand, if great accuracy is desired, it would be folly to attempt to attain it by measurement of gas volumes over water.

[80] See Ott, p. 161.

a moment from time to time to relieve the excess pressure due to the expansion of the nitrogen in the tube. The heating is continued until the thermometer shows a temperature of 270° and the tube is kept at about this temperature during the combustion. The pinchcock *F* is once more opened to bring the nitrogen in the combustion tube to atmospheric pressure and the burette is then connected with the bent capillary tube. The pinchcocks *E, F,* and *G* are now opened and the gas mixture in the burette is *slowly* passed through the combustion tube into the water pipette. If the gas is passed through the tube at the rate of about 10 cc. per minute, it has been found that four or five passages of the gas will completely remove the hydrogen from 100 cc. of a gas mixture that contains 40 per cent of this gas. With a higher percentage of hydrogen, or in fact in any case, the gas should be passed backward and forward through the combustion tube until two successive readings are the same. After the removal of the hydrogen is completed, the gas is drawn back into the burette until the water in the capillary of the pipette stands at the original height and the pinchcock *G* is then closed. The temperature of the combustion tube is now brought again to exactly 270°, and the pinchcock *E* is closed. The gas is allowed to stand in the burette for two minutes to come to the temperature of the surrounding water, and its volume is then read. The contraction in volume shows directly the amount of hydrogen.

If it is desired to determine methane in the gas residue in the burette, the water pipette is replaced by a combustion pipette (Fig. 66) that is filled with water[81] and that contains a measured amount of oxygen, about 100 cc. The terminals of the pipette are connected with a source of electric current, the current is turned on, and the spiral is heated to dull redness. The combustion tube of copper oxide is kept at about 270°. The level-bulb of the pipette is placed upon the top of the stand *S*, with the pipette. A Hofmann detachable screw pinchcock is placed upon the rubber tube that connects the burette with its level-tube; the level-tube of the burette is then brought to such height that the confining liquid in it stands but slightly higher than the confining liquid in the burette, and the screw pinchcock is now closed. The level-tube is placed upon the top of another wooden stand. The pinchcocks *E*, *F*, and *G* are opened and set back on the glass tubes. The screw pinchcock is then very carefully opened, and the gas in the burette is very slowly started over through the tube of copper oxide into the combustion pipette. When the water in the burette has risen to the top of the burette, all the pinchcocks are closed, and the burette is disconnected from the small capillary tube at *E*. The burette is then connected to a phosphorus pipette[82] containing nitrogen and a known volume, from 15 to 20 cc., of nitrogen is drawn into the burette. The burette is then disconnected from the phosphorus pipette and is again connected to the small capillary at *E*. The pinchcocks *E*, *F*, and *G* are opened, and the gas forced from the burette through the tube of copper oxide into the combustion pipette as before. When the water in the burette reaches the top of the burette the pinchcock *E* is closed, and the tube of copper oxide is again brought to atmospheric pressure by proper adjustment of the height of the level-bulb of the pipette and the pinchcock *G* is then closed. The burette and the combustion pipette are disconnected from the tube of copper oxide and the burette is joined directly to the combustion pipette by a capillary tube of the usual form. The gas is drawn from the combustion pipette into the burette and is then passed into a pipette containing a solution of potassium hydroxide to remove carbon dioxide. The residual gas is now brought back into the burette, and is again measured. To ascertain the volume of methane in the sample, add the volume of gas remaining after the determination of hydrogen to the sum of the oxygen introduced into the combustion pipette and the volume of nitrogen used for sweeping the residual gas out of the tube of copper oxide. From this sum, deduct the final volume of the gas that remains in the burette after the absorption of the carbon dioxide formed in the combustion of the methane. One-third of this result is the volume of the methane in the gas sample.

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[81] Mercury may of course be used.

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[82] See note 80, p. 167.

CHAPTER XIV

PROPERTIES OF THE VARIOUS GASES AND METHODS FOR THEIR DETERMINATION

OXYGEN

Properties of Oxygen. — Specific gravity (air = 1), 1.1053;[1] density at 0°, 760 mm., 1.4290 grams per liter; critical temperature, —118.8°; critical pressure, 49.7 atmospheres; melting point, —218.4°; boiling point, —183.0°.

Oxygen is but slightly soluble in water. The solubility of oxygen in one liter of water that is in contact (a) with atmospheric air, and (b) with pure oxygen, at 760 mm. pressure is as follows:

Temperature	Air (cc.)	Oxygen (cc.)
0°	10.19	48.89
5°	8.91	42.87
10°	7.87	38.02
15°	7.04	34.15
20°	6.36	31.03
25°	5.78	28.31
30°	5.26	26.08

Detection and Determination of Small Quantities of Oxygen.—Several methods have been proposed for the detection and determination of small quantities of oxygen. Pfeiffer[2] described a colorimetric method of detection which is based on the color formed when a solution of caustic potash is brought into contact with pyrogallol in the presence of oxygen. By comparing the color formed with that of a 0.1 normal iodine solution, the method may be made quantitative. Lubberger[3] brings the gas mixture into contact with alkali and manganous hydrate. After adding potassium iodide and acidifying, the liberated iodine, equivalent to the oxygen, is titrated with sodium thiosulphate. This method has been modified by Hand[4] who adds starch and determines the oxygen colorimetrically. Schmalfuss and Werner[5] describe a method for the detection of oxygen which depends upon the fact that a piece of filter paper moistened with a drop of a one per cent solution of diphenylamine in 18 N sulphuric acid and exposed to nitric oxide becomes blue in the presence of oxygen. A solution of α-naphthylamine in dilute acetic acid may also be used. Hofer and Wartenburg[6] determine small quantities of oxygen by the color produced when the gas mixture is passed through a solution of indigo carmine reduced with sodium hyposulphite.

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[1] These values are from either Landolt and Börnstein's *Physikalisch Chemische Tabellen* or the *International Critical Tables.*

[2] *J. Gasbel.*, **40**, 354 (1897).

[3] *J. Gasbel.*, **41**, 695 (1898).

Determination of Oxygen.—Oxygen may be determined either by mixing it with an excess of hydrogen and exploding the mixture, or by passing the gas into a combustion pipette containing an excess of hydrogen, or by bringing it into contact with glowing metallic copper, or by absorption of the gas.

DETERMINATION OF OXYGEN BY COMBUSTION.—The explosion analysis may be carried out in the apparatus described on page 138.

The determination by combustion may conveniently be made with the pipette shown in Fig. 66. Greenwood and Zealley[7] have described an apparatus working on this principle for the automatic determination of small amounts of oxygen in combustible gas mixtures. The oxygen may also be determined by combustion[8] over a heated platinum wire as described on page 150.

In all of these methods two volumes of hydrogen unite with one volume of oxygen to form liquid water. The volume of oxygen present is consequently equal to one-third of the contraction of the gas volume.

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[4] *J. Chem. Soc.*, **123**, 2573 (1923).

[5] *J. prakt. Chem.*, **111**, 62 (1925).

[6] *Z. angew. Chem.*, **38**, 9 (1925).

[7] *J. Soc. Chem. Ind.*, **38**, 87 (1919).

[8] Geissler, *Z. angew. Chem.*, **38**, 948 (1925); Steuer, *Chem. Ztg.*, **49**, 713 (1925).

The hydrogen needed for these analyses may be prepared as described on page 142 or it may be generated by the electrolysis of water in the Bunsen apparatus,[9] in which the positive pole consists of a zinc wire floating in mercury. In the determination of oxygen by explosion with hydrogen, the oxygen should be mixed with from three to ten times its volume of hydrogen. If the amount of oxygen in the original gas mixture is quite low, there should be added, in addition to the hydrogen, an amount of oxyhydrogen gas sufficient to render the mixture explosive.

Larson and White[10] give a method for the determination of very small quantities of oxygen in hydrogen. The gas mixture is passed over a platinized platinum catalyst at 275° to 300°, and the rise of temperature due to the combustion is measured by means of a thermo-element. According to the authors, this method is capable of determining 0.001 per cent of oxygen with an accuracy of 3 per cent.

DETERMINATION OF OXYGEN WITH COPPER EUDIOMETER.—Very accurate determinations of oxygen may be made by combustion with copper. Kreusler has so improved the apparatus devised by Ph. v. Jolly[11] for the determination of oxygen in the atmosphere that it is now one of the most exact methods known. A so-called copper eudiometer, whose construction is based upon his well-known air thermometer, is used for the determination. The air whose oxygen contents is to be determined is admitted into a bulb that has previously been completely exhausted, and the pressure is read off on a very exact mercury manometer. The oxygen is then absorbed by a copper spiral that is heated to glowing by a strong electric current; the metallic copper is changed to cuprous and cupric oxide. After the apparatus has become cool, the remaining nitrogen is brought to the initial volume by changing the pressure, and a reading is taken of the pressure now prevailing.[12] When due regard is given to all the necessary precautions, the method is of the greatest exactness; it is, however, very complex and tedious, and for this reason is not well suited to the making of a large number of determinations.

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[9] Bunsen, *Gasometrische Methoden* (1877), p. 80.
[10] *J. Am. Chem. Soc.*, **44**, 20 (1922).
[11] *Wied. Ann. N.F.*, **6**, 520 (1879).

DETERMINATION OF OXYGEN BY ABSORPTION.—Oxygen may rapidly and accurately be determined by means of various absorbents, among the best of which are—

1. A strongly alkaline solution of pyrogallol; 2. Phosphorus; 3. Copper; 4. Solutions of ferrous salts; 5. Sodium hyposulphite; 6. Chromous chloride.

1. Alkaline Pyrogallol

The discovery of the absorption of oxygen by an alkaline solution of pyrogallol is generally attributed to Döbereiner,[13] but Liebig [14] was the first to utilize this reaction for the quantitative removal of oxygen from a mixture of gases. He employed a solution of potassium hydroxide of sp. gr. 1.4, and added to it one-half its volume of a solution of one gram of pyrogallol in 5 to 6 cc. of water. Later Weyle and Zeitler [15] studied the effect of the concentration of the alkali upon the absorbing power of the reagent and showed that the absorption is a function of the alkalinity. They found that a solution of potassium hydroxide of sp. gr. 1.05 gives the reagent its greatest absorbing power, and that in solutions of higher concentration of alkali the absorbing power is lessened. Similar experiments were performed by Weyle and Goth [16] with the substitution of sodium hydroxide and sodium carbonate for the potassium hydroxide.

Shortly after Liebig's experiments it was found [17] that during the oxidation of alkaline pyrogallol, a small quantity of carbon monoxide may be formed, depending upon the energy of the oxidation. Poleck,[18] in his researches on the composition of the air, carefully examined this source of error and was unable to find even traces of carbon monoxide when oxygen is absorbed by an alkaline solution of pyrogallol.

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[12] Kreusler, *Ueber den Sauerstoffgehalt der atmosphärischen Luft. Landwirthschaftliche Jahrbücher*, **14**, 305 (1885).

[13] *Gilbert's Ann.*, **74**, 410 (1823).

[14] *Liebig's Ann.*, **77**, 107 (1851).

[15] *Liebig's Ann.*, **205**, 255 (1880).

[16] *Ber.*, **14**, 2659 (1881).

[17] Calvert, *Compt. rend.*, **57**, 873 (1863); Cloëz, *ibid.*, **57**, 875 (1863); Boussingault, *ibid.*, **57**, 885 (1863).

Speck[19] recommends the use of barium hydroxide in place of potassium hydroxide to prevent the formation of carbon monoxide.

Hempel,[20] in his researches on the composition of air, employed a solution prepared by mixing one volume of a 25 per cent solution of pyrogallol with six volumes of a 60 per cent solution of potassium hydroxide. The solution is brought into a double absorption pipette (Fig. 39) or, if many determinations are to be made by the "exact" method, the solution is kept in an apparatus[21] designed especially for this purpose. Hempel states that a solution prepared as above gives off no carbon monoxide during the absorption, or at most only such slight amounts that the error thus caused falls within the limit of error of the readings.

The determination should not be made at a temperature much below 15°, for the absorption by alkaline pyrogallol is very much less active at a temperature under 7°. At a temperature of 15° or higher, the last trace of oxygen can be removed with certainty in the space of three minutes by shaking with the solution of alkaline pyrogallol, while at lower temperatures the absorption is not complete after six minutes.

Two years later Hempel[22] used an alkaline solution of pyrogallol prepared by dissolving 120 grams of potassium hydroxide in 80 cc. of water and adding to this 5 grams of pyrogallol dissolved in 15 cc. of water. He points out that potassium hydroxide purified by alcohol should not be employed in the preparation of alkaline pyrogallol. Still later he recommended [23] a solution prepared by dissolving 15 grams of pyrogallol in 15 cc. of water and mixing this with 135 cc. of saturated solution of potassium hydroxide.

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[18] *Z. anal. Chem.*, **8**, 45 (1869).

[19] *Schriften der Gesellschaft zur Beförderung der gesammte Naturwissenschaft zu Marburg*, **10** (1871).

[20] *Ber.*, **18**, 267, 1800 (1885).

[21] Hempel, *loc cit.;* Dennis, *Gas Analysis* (1913), p. 162.

[22] *Ber.*, **20**, 1864 (1887).

However, Lewes [24] states that a solution prepared by adding 10 grams of pyrogallol to 150 cc. of a 20 per cent solution of sodium hydroxide must not be employed for the absorption of oxygen more than four or five times, because it then begins to form carbon monoxide.

Clowes [25] found that a solution containing 10 grams of pyrogallol and 24 grams of potassium hydroxide in 100 cc. of solution could be used to determine oxygen when the latter does not exceed 28 per cent of the total volume, but that with richer mixtures carbon monoxide is formed unless a much stronger solution of potassium hydroxide is employed. Berthelot [26] states that a large excess of alkali and pyrogallol, sufficient to absorb four or five times the amount of oxygen present, is necessary to prevent the formation of more than a negligible quantity of carbon monoxide. He studied the effect of the replacement of the potassium hydroxide by sodium hydroxide, barium hydroxide, and ammonium hydroxide, and found that the total amount of oxygen that was absorbed by the solution containing sodium hydroxide was practically the same as with the use of potassium hydroxide, while with barium hydroxide the absorption was less. Ammonium hydroxide gave a greater absorption. The effect of these substitutions upon the formation of carbon monoxide was small.

Benedict,[27] in his precise determinations of the oxygen content of the atmosphere, observed that the results depend upon the concentration of the alkali used. He is of the opinion that the discrepancy in the results obtained with various solutions may be due to the formation of carbon monoxide. He recommends that the absorbent be prepared as follows: 500 grams of stick potassium hydroxide, not purified by alcohol, is dissolved in 250 cc. of water. The specific gravity of the solution is usually 1.55, but, if it varies materially from this figure, more potassium hydroxide or more water is added until the density of 1.55 is reached. 135 cc. of this solution is added to a solution of 15 grams of pyrogallol in 15 cc. of distilled water.

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[23] Hempel, *Gasanalytische Methoden* (1913), p. 132.

[24] *J. Soc. Chem. Ind.*, **10**, 407 (1891).

[25] *Chem. News*, **72**, 288 (1895); **74**, 199 (1896); *J. Soc. Chem. Ind.*, **15**, 170 (1896).

[26] *Ann. chim. phys.*, [7] **15**, 294 (1898); *Compt. rend.*, **126**, 1066, 1459 (1898).

[27] Benedict, *The Composition of the Atmosphere* (1912), p. 113.

Benedict obtained the highest results for oxygen with a solution prepared as directed by Haldane,[28] containing one gram of pyrogallol to 10 cc. of potassium hydroxide of sp. gr. 1.55. Haldane states that the solution prepared according to his directions yields no carbon monoxide on the absorption of oxygen.

The use of an alkaline solution of pyrogallol for the absorption of oxygen was investigated by Anderson[29] who found, after consideration of the various factors which determine the desirability of this reagent for general use, that a solution prepared by dissolving 15 grams of pyrogallol in 100 cc. of a solution of potassium hydroxide of sp. gr. 1.55 is the most desirable. This solution gave a specific absorption of 25 at 20° to 24° on one-minute shaking in a Hempel double pipette for liquid reagents, the sample containing 20.9 per cent of oxygen. He concludes that if any carbon monoxide is formed, the amount is too small to cause appreciable error even when the reagent is almost exhausted. Hempel's objection to the use of potassium hydroxide purified by alcohol does not appear to be valid, and the substitution of sodium hydroxide for potassium hydroxide is not practicable. He investigated[30] the specific absorption of this solution, and found that it is not well suited for use in pipettes designed for the absorption of oxygen without shaking, nor can it be adapted for convenient use in such pipettes without considerable loss in specific absorption. On further investigation,[31] he discovered that by modifying the form of the pipette (see Fig. 41), it was possible to employ a reagent containing a higher concentration of pyrogallol, and he recommends a solution containing 25 grams of pyrogallol dissolved in 100 cc. of a solution of potassium hydroxide of sp. gr. 1.55. The specific absorption of this reagent for one-minute contact is about 36 when used in the modified pipette at 20° to 24° C. with gas samples 100 cc. in volume containing 20.9 per cent of oxygen.

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[28] Haldane, *Methods of Air Analysis* (1912), p. 13.
[29] *Ind. Eng. Chem.*, **7**, 587 (1915).
[30] Anderson, *Ind. Eng. Chem.*, **8**, 131 (1916).

The investigation of Henrich [32] showed that alkaline solutions of pyrogallol prepared with potassium hydroxide absorb oxygen more readily than those prepared with sodium hydroxide. He also investigated the absorption capacity of solutions of hydroxyquinol. A solution prepared by suspending 11.4 grams of triacetyl hydroxyquinol in 20 cc. of water, adding a concentrated solution of potassium hydroxide containing 17.5 grams of potassium hydroxide and diluting with 130 cc. of water, absorbed the oxygen completely from one hundred cc. of air on vigorous shaking for one-half minute. The absorption capacity of this solution was unaltered on standing for some months.

Since numerous workers had advocated the use of sodium hydroxide in preparing alkaline pyrogallol solutions, Shipley [33] investigated this to determine whether sodium pyrogallate might be substituted for potassium pyrogallate in the absorption of oxygen from gas mixtures. He found that complete absorption of the oxygen was secured in four minutes from a number of solutions containing pyrogallol, sodium hydroxide, and water in varying proportions. No carbon monoxide was formed during the absorption, and the specific absorption of a solution consisting of 10 cc. of sodium hydroxide solution (1:1), 4 cc. of water, and 10 grams of pyrogallol was found to be five times that of the potassium pyrogallate solution recommended by Anderson.[34] The total volume of oxygen absorbed was in excess of the proportion of three atoms of oxygen for each molecule of pyrogallol. He also found that for general use in gas analysis, ammonium and barium pyrogallate were impracticable.

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[31] Anderson, *Ind. Eng. Chem.*, **8**, 133 (1916).

[32] *Ber.*, **48**, 2006 (1915).

[33] *J. Am. Chem. Soc.*, **38**, 1687 (1916).

This investigation showed that the best sodium reagent is superior to the best potassium reagent as regards specific absorption and cost of materials, and is inferior as regards the time for complete absorption and the convenience of manipulation. However, on consideration of the relative importance of these points of superiority and inferiority, Anderson[35] concludes that true economy dictates that potassium hydroxide should be employed in preference to sodium hydroxide for the preparation of alkaline pyrogallol solution.

Jones and Meighan[36] have thoroughly investigated the efficiency of sodium pyrogallate solutions and find that the rate of oxygen absorption increases with the dilution of the sodium hydroxide and is proportional to the concentration of the pyrogallol for any given concentration of sodium hydroxide. Solutions of sodium pyrogallate, prepared by using solutions of sodium hydroxide of specific gravity less than 1.30, give off carbon monoxide, and all sodium pyrogallate solutions give off carbon monoxide when used in analyzing gas samples containing more than 95 per cent oxygen. They state that the solution recommended by Shipley is too viscous, and they recommend a solution prepared by mixing 5 parts of a solution of sodium hydroxide containing stick sodium hydroxide dissolved in an equal weight of water, with 2 parts of a solution of pyrogallol containing one gram of pyrogallol dissolved in 3 cc. of water. This solution has a fairly high rate of absorption and gives off a minimum quantity of carbon monoxide. In a recent investigation of the absorption of oxygen and the liberation of carbon monoxide by alkaline pyrogallol solutions, Drakeley and Nicol[37] found that while potassium hydroxide offers no advantage over sodium hydroxide so far as the prevention of the formation of carbon monoxide is concerned, concentrated solutions of it can be more easily manipulated in gas analysis. The production of carbon monoxide was minimized by using a highly concentrated solution, agitating the solution, and diluting the gas mixture with nitrogen so that it does not contain over 25 per cent oxygen. The solution of pyrogallol should be nearly fresh, since the formation of carbon monoxide increases as the solution becomes exhausted. All solutions of pyrogallol that were investigated evolved carbon monoxide when pure oxygen was absorbed. The best solution for general use, according to Drakeley and Nicol, is that recommended by Anderson[38] and this gives good results if the solution of pyrogallol is in considerable excess, is agitated vigorously during the absorption, is not used after it has absorbed one-tenth its specific absorption volume, and if the oxygen content of the gas mixture being analyzed is not over 25 per cent. However, for an accurate determination of oxygen by alkaline pyrogallol, it is essential to remove the carbon monoxide before taking the final reading.

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[34] *Ind. Eng. Chem.*, **7**, 587 (1915).
[35] *Ind. Eng. Chem.*, **8**, 999 (1916).
[36] *Ind. Eng. Chem.*, **11**, 311 (1919).

Neumann and Steuer[39] also are of the opinion that solutions prepared with potassium hydroxide are better than those prepared with sodium hydroxide, and they state that in the absorption of oxygen from commercial oxygen by an alkaline solution of pyrogallol, carbon monoxide is always formed. If the carbon monoxide is removed, then correct values for the nitrogen content will be obtained.

Etelka von Kovacs-Zorkoczy[40] states that the absorption is proportional to the concentration of the pyrogallol, 2 gram molecules of pyrogallol absorbing 5 atoms of oxygen. This absorption is independent of the nature and concentration of the alkali used and of the partial pressure of the oxygen.

[37] *J. Soc. Chem. Ind.*, **44**, 457 (1925).
[38] *Ind. Eng. Chem.*, **7**, 587 (1915).
[39] *Chem. Ztg.*, **49**, 585 (1925).
[40] *Biochem. Z.*, **162**, 161 (1925).

From the authors' experience, the solution recommended by Anderson containing 15 grams of pyrogallol in 100 cc. of a solution of potassium hydroxide of specific gravity 1.55, is the most satisfactory for general use. The objection has been offered to this concentrated solution that a precipitate forms which chokes the glass tubes. No such difficulty has been experienced in the Cornell laboratory with this reagent when using the special pipette designed by Anderson (see Fig. 41). In fact, he recommends even a more concentrated solution for this pipette. The reagent must be protected from the air when not in use and of course carbon dioxide must previously be removed before the absorption of oxygen.

2. Phosphorus

The use of phosphorus for the determination of oxygen was probably first employed by Scheele in the phosphorus eudiometer. Following this, many investigators, including Lavoisier, used this method to determine the oxygen content of air. Brunner and others passed the air over phosphorus and determined the oxygen by the increase in weight of the phosphorus.

The method of Lindemann[41] for the absorption of oxygen by solid phosphorus gives, under proper conditions and in the absence of gases that inhibit the reaction, very accurate results. The amount of phosphorus contained in a Hempel gas pipette is capable of absorbing a very large volume of oxygen, in which respect it is superior to alkaline pyrogallol which has a relatively small absorbing power.

Phosphorus does not, however, unite with oxygen when the gas has a high partial pressure. If the oxygen is nearly pure, no reaction takes place between it and phosphorus, and only when its pressure is lowered either by dilution with another gas, or by partial exhaustion with an air-pump, does a union of the phosphorus and oxygen result. The reaction between the two elements is explosive in character when the gas mixture contains from 50 to 75 per cent of oxygen, but it proceeds quietly when less than 50 per cent of oxygen is present. It is unsafe to use the method for the determination of oxygen in gas mixtures that contain enough hydrogen to render them explosive, because the rise of temperature caused by the interaction of the phosphorus and oxygen may ignite the mixture. In such case, or when the mixture contains over 50 per cent of oxygen, the gas should be absorbed by some agent other than phosphorus.

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[41] *Z. anal. Chem.*, **18**, 158 (1879).

The union of phosphorus with oxygen is prevented or greatly retarded by the presence of even small amounts of certain other gases, such as hydrogen sulphide, ethylene, acetylene, some other hydrocarbons, some ethereal oils, alcohol or ammonia.

The reaction is further dependent upon the temperature. It proceeds normally at about 20° C., while at 14° it takes place quite slowly, so that a quarter of an hour or longer is required to completely separate the oxygen from 100 cc. of air. At 10° and still lower temperatures a half-hour's time would not be sufficient. It follows from this that during the colder months of the year the absorption must be carried out in warm rooms.

The absorption of oxygen by phosphorus may conveniently be effected by passing the gas mixture into a Hempel simple pipette for solid and liquid reagents (Fig 38) that contains sticks of phosphorus immersed in water.

Phosphorus may be purchased on the market in the form of thin sticks ready for use, or it may be prepared by the analyst himself in this form in the following manner: A test tube is filled with water, and sticks of phosphorus of the ordinary commercial size are introduced into the tube. The tube is then placed in a metal water bath in which the temperature of the water is maintained at about 50°. The phosphorus readily melts and it is protected from the action of the air by the water above it. Enough phosphorus should be used to form in the test tube a column of molten phosphorus about 7 cm. high. A 2-liter beaker full of cold water is placed near the water bath. A glass tube with slight taper and about 3 mm. internal diameter is then pushed down to the bottom of the test tube containing the molten phosphorus, the upper end of the tube is closed with the moistened finger, and the tube, carrying a column of the molten phosphorus with a little water above it, is quickly lifted out of the test tube and dipped into the beaker of cold water. If the wall of the glass tube is not too thick, the phosphorus soon solidifies and since it decreases in volume on changing from the liquid to the solid state, the stick will usually fall out of the tube of itself. If it adheres to the walls it may easily be pushed out with a wire. The cylindrical part of the gas pipette in which the phosphorus is to be placed should be of brown glass to protect the phosphorus from the action of the light (see p. 63). If such pipettes are not available, the whole pipette when not in use should be covered by a light-tight box of wood or cardboard. The pipette is filled by turning it upside down, removing the stopper of the cylindrical portion, filling the cylinder with water, and then introducing the small sticks of phosphorus until the cylinder is tightly packed with them. The stopper of the cylinder is then inserted and the pipette is turned into upright position.

The surface of the yellow sticks of phosphorus becomes covered by a thin layer of red phosphorus on exposure to light, which interferes with the absorption of oxygen. Such sticks should be removed from the pipette, melted under water, skimmed and cast into new sticks. Holmes[42] suggests that this inactive layer be removed by treatment with nitric acid, but Henwood[43] states that such treatment may result in an explosion.

In the absorption of oxygen, the water in the pipette is first driven up in the capillary and to the end of the connecting bent capillary tube by blowing into a rubber tube attached to the wide tube of the end bulb. The connecting capillary tube is then inserted into the rubber tube of the burette and the gas mixture is passed over into the phosphorus pipette, the water or mercury from the burette being allowed to follow nearly to the cylinder of the pipette. The union of the phosphorus with the oxygen is complete in three minutes or less, the end of the reaction being shown by the disappearance of the glow when the pipette is in a dark room. Inasmuch as the different oxidation products of phosphorus are soluble in water, the surface of the sticks of phosphorus is freed from these substances by the solvent action of the confining water provided the water is renewed from time to time.

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[42] *Ind. Eng. Chem.*, **15**, 357 (1923).

[43] *Ind. Eng. Chem.*, **15**, 650 (1923).

Travers[44] proposed the absorption of oxygen by vapor of phosphorus, and this method was later used by Watson[45] and Aston[46] in the determination of the oxygen content of the air.

Centnerszwer[47] employs a solution of phosphorus in castor oil as an absorbent for oxygen in gas analytical work. This solution has been studied by Anderson and Biedermann[48] who found that the absorption of oxygen took place slowly and was not complete in a reasonable length of time. They add that the reagent is not suitable for the determination of oxygen at ordinary temperatures, and that there seems to be no reason why it should be preferred to an alkaline solution of pyrogallol.

3. Copper

It has long been known that copper can be used for the determination of oxygen. In the determination of oxygen in air, von Jolly absorbed the oxygen by a glowing copper spiral (see p. 173). Doyère[49] used an ammoniacal solution of copper chloride, and Schlösing[50] employed copper immersed in an ammoniacal solution of ammonium chloride.

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[44] Travers, *The Experimental Study of Gases* (1901), p. 83.
[45] *J. Chem. Soc.*, **99**, 1460 (1911).
[46] *Ibid.*, **115**, 472 (1919).
[47] *Chem. Ztg.*, **34**, 494 (1910).
[48] *Ind. Eng. Chem.*, **8**, 135 (1916).
[49] *Ann. chim. phys.*, [3], **28**, 5 (1850).
[50] *Chem. Zentr.*, **14**, 678 (1869).

Hempel[51] states that a very rapid and complete absorption of oxygen results when the gas is brought into contact with metallic copper in the form of little rolls of wire-gauze immersed in a solution consisting of equal parts of a saturated solution of ammonium carbonate and ammonium hydroxide of 0.93 specific gravity.

Such an ammoniacal solution has a tension that may in most cases be disregarded, and, provided the absorption apparatus contains sufficient metallic copper, the solution can easily absorb 24 times its volume of oxygen. Since the surface of metallic copper is frequently covered with a thin layer of grease, it is necessary to clean it before using by exposing it for a moment to the action of nitric acid.

The method described admits of a very rapid and exact determination of oxygen. As compared with alkaline pyrogallol, copper has a much greater absorbing power for oxygen, and it has the advantage over phosphorus, aside from the danger attending the use of the latter, of absorbing equally well at any temperature.

In the analysis of gas mixtures that contain carbon monoxide the method cannot be used, because the basic ammonium cuprous carbonate, formed from the copper present, absorbs carbon monoxide.

This reagent has been used in a portable apparatus[52] for testing oxygen, and by Van Brunt[53] to absorb the oxygen from air in a nitrogen generator.

Badger[54] made a careful study of the proper concentration of this reagent and the best ammonium salt for its preparation. and states that the solution of Hempel is not satisfactory. He recommends a solution prepared by saturating with ammonium chloride a mixture of one part of concentrated ammonium hydroxide and one part of water. This solution has a specific absorption of fifty to sixty volumes and then fails, not by refusing to absorb quantitatively, but by the formation of so heavy a precipitate that it becomes unmanageable. The presence of metallic copper in the gas space is essential for complete absorption of the oxygen. In the analysis of commercial oxygen, where the residue of unabsorbed gas is very small, care must be taken that one or two copper wires project up into the entrance of the capillary. Otherwise some of the gas may not come into contact with the metallic copper and the last traces of oxygen may then escape absorption.

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[51] Hempel, *Gasanalytische Methoden* (1913), p. 141.
[52] *Iron Age*, **94**, 879 (1914).
[53] *J. Am. Chem. Soc.*, **36**, 1448 (1914).
[54] *Ind. Eng. Chem.*, **12**, 161 (1920).

A special apparatus consisting of a pipette and a burette, the upper part of which is a tube of small diameter, has been suggested by the Air Reduction Company for the analysis of commercial oxygen using this reagent.

The reagent is used in the same manner as solid phosphorus, in a pipette for solid absorbents. In making the absorption, the gas is shaken in the pipette with the reagent for five minutes. The oxygen is absorbed by the exposed surface of the moist copper, the sub-oxide that is formed being afterwards dissolved by the ammoniacal solution. Badger states that the reagent is cleaner to use and has a longer life than alkaline pyrogallol; it is active at any temperature, and is not affected by poisons which interfere with the absorption by phosphorus. Ammonia may be given off from the reagent, especially when fresh, so that it is necessary to pass the gas into the pipette containing dilute sulphuric acid before determining the decrease in volume due to the removal of the oxygen. This solution absorbs carbon monoxide and acetylene, and therefore cannot be used to determine oxygen when these gases are present.

4. Solutions of Ferrous Salts

The oxygen in gas mixtures containing carbon monoxide can be removed according to de Koninck,[55] by an alkaline solution of ferrous tartrate. Kostin[56] removes the oxygen by the use of a pipette filled with iron wire-gauze that stands in a saturated solution of ferrous sulphate to which has been added one-third of its volume of strong ammonium hydroxide. Neither of these solutions is very efficient for the absorption of oxygen.

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[55] *Z. angew. Chem.*, **3**, 727 (1890).

[56] *Arch. ges. Physiol.*, **83**, 572 (1901).

5. *Sodium Hyposulphite*

Sodium hyposulphite was apparently first employed by Pettersson and Högland[57] in their determinations of the oxygen content of air. Franzen[58] later examined the substance with a view to ascertaining whether it could be used in gas analysis for the absorption of oxygen. He prepares the reagent by dissolving 50 grams of sodium hyposulphite in 250 cc. of water, and 30 grams of sodium hydroxide in 40 cc. of water, and mixing the two solutions. This final solution is placed in a Hempel pipette for solid reagents that has first been filled with small rolls of iron wire-gauze. Franzen states that in this apparatus oxygen, if present in not too large amount, is completely absorbed in five minutes. The reaction that takes place is represented by the equation

$$2Na_2S_2O_4 + 2\ H_2O + O_2 = 4\ NaHSO_3,$$

from which it appears that one gram of sodium hyposulphite is able to absorb about 64 cc. of oxygen. One cc. of the above solution will consequently absorb 10.7 cc. of oxygen. Franzen enumerates the following advantages possessed by sodium hyposulphite over other absorbents for oxygen. In the first place it is decidedly cheaper than pyrogallol; secondly, it absorbs oxygen as rapidly at low temperatures as it does at higher, whereas the absorbing power of alkaline pyrogallol and of phosphorus shows marked decrease with fall of temperature. Furthermore the absorption of oxygen by the reagent is not influenced by gases that prevent the oxidation of phosphorus.

Henrich[59] states that if potassium hydroxide is used instead of sodium hydroxide in this alkaline solution of sodium hyposulphite, the absorption of oxygen occurs much more rapidly.

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[57] *Ber.*, **22**, 3324 (1889).

[58] *Ber.*, **39**, 2069 (1906); Durig, *Biochem. Z.*, **4**, 65 (1907).

[59] *Ber.*, **48**, 2006 (1915).

In a recent investigation of this absorbent, Fieser[60] found that the rapidity of the absorption is increased by addition of a small quantity of sodium anthraquinone-β-sulphonate which gives to the solution a deep red color. He recommends for use in an ordinary pipette a solution containing 16 grams of sodium hyposulphite, 3.3 grams of stick sodium hydroxide, and 2 grams of anthraquinone-β-sulphonate, in 100 cc. of water. This solution absorbs the oxygen from air completely on one minute's shaking, and from a sample containing 90 per cent of oxygen completely on two minutes' shaking. The solution is cheap, easy to handle, does not evolve carbon monoxide, and the exhaustion of the reagent is indicated by a color change. However, Kruse[61] found upon investigation of this solution that the absorption is accompanied by slight frothing and that the reagent is not as suitable as pyrogallol, because the absorption becomes sluggish within fourteen days.

6. Chromous Chloride

Chromous chloride was proposed by von der Pfordten[62] as an absorbent for oxygen in the presence of hydrogen sulphide. Numerous investigators, however, state that as an absorbent for oxygen it is open to objection because it easily gives off hydrogen. Anderson and Riffe[63] have investigated the solution employed by von der Pfordten and found that it is unsatisfactory for gas-analytical work. By another method of preparation they secured a stable solution, but the absorption of oxygen although rapid is not complete. They state that it is improbable that chromous chloride will ever be widely used in gas analysis except for the absorption of oxygen in the presence of carbon dioxide and hydrogen sulphide.

[60] *J. Am. Chem. Soc.*, **46**, 2639 (1924); *Science*, **59**, 560 (1924).
[61] *J. Pharmacol. Proc.*, **25**, 151 (1925).
[62] *Liebig's Ann.*, **228**, 112 (1885).
[63] *Ind. Eng. Chem.*, **8**, 24 (1916).

OZONE

Properties of Ozone.—Specific gravity (air = 1), 1.624, density at — 80°, 760 mm., 3.0000 grams per liter; critical temperature, — 5.0°; critical pressure, 67 atmospheres; melting point, — 251°; boiling point, — 112°.

Ozone, O_3, is, at ordinary temperatures, a gas that possesses a peculiar, pungent odor which is noticeable even when only one part is present in 500,000 parts of air. The odor thus furnishes one of the most delicate tests for ozone.[64] In a layer one meter thick, ozone has a distinctly blue color. It exercises a markedly irritating effect on the mucous membrane, and is a powerful oxidizing agent.

The Detection of Ozone.—The detection of ozone, particularly in such small amounts as may be present in atmospheric air, has frequently been the subject of investigation, and many agents and many methods for accomplishing the object have been described in the chemical journals. It has been found particularly difficult to identify, in the presence of one another, the three gases ozone, nitrogen peroxide, and hydrogen dioxide.

One of the oldest tests for ozone in air consists in exposing to the atmosphere a paper which has been dipped into a solution of potassium iodide and starch.[65] However, the blue color formed in this case, as well as with guiacum tincture,[66] is not characteristic of anything more than an oxidizing gas, as it will also be produced by nitrogen peroxide, hydrogen peroxide, chlorine, and bromine. Houzeau[67] suggested the use of red litmus paper moistened with potassium iodide where the alkali formed by the ozone turns the paper blue. This test is unsatisfactory because the liberated iodine gives a brown color which masks the blue color due to the alkali. Even in solution a coloration is produced which renders the test unsatisfactory. Tetramethylparaphenylenediamine[68] is also turned blue by all oxidizing gases. Moreover, nitrogen peroxide gives the same color as ozone, and all oxidizing gases give yellowish colors with this substance.[69]

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[64] Pring, *Chem. News,* **109,** 73 (1914).

[65] Schönbein, *Verh. Nat. Ges. Basel,* **4,** 58 (1842); *J. prakt. Chem.,* [1] **84,** 193 (1861).

[66] Struve, *Z. anal. Chem.,* **8,** 315 (1869).

[67] *Compt. rend.,* **74,** 712 (1872).

Engler and Wild[70] test for the presence of ozone by passing large quantities of the air under examination through finely divided chromic acid to remove any hydrogen peroxide, and then into a glass tube in which are placed, side by side, a manganous sulphate paper which is colored brown by ozone but not by chlorine, and a thallous oxide paper which remains colorless in the presence of nitrous acid but is turned brown by ozone. The coloration of both papers shows the presence of ozone.

Silver foil[71] is not satisfactory because it is not sensitive.

Arnold and Mentzel[72] recommend the use of an alcoholic solution of benzidine or, still better, an alcoholic solution of tetramethyl-p-p-diaminodiphenylmethane. The former gives a brown color with ozone, blue with nitrogen peroxide, and is unchanged by hydrogen peroxide. The latter gives a violet color with ozone, yellow with nitrogen peroxide, whereas with hydrogen peroxide it remains unchanged. Fischer and Marx[73] have also used this latter reagent for the detection of ozone, and they recommend the use of liquid air to separate and detect small quantities of the oxides of nitrogen in the presence of ozone. Hayhurst and Pring[74] found that this test is not a delicate one and that the blue and yellow colors due to oxides of nitrogen appear to mask the effect of ozone.

Keiser and McMaster[75] found that potassium permanganate, even in very dilute solution, is not decolorized by ozone.

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[68] Wurster, *Ber.*, **19**, 3195 (1896).

[69] Erlwein and Weyl, *Ber.*, **31**, 3158 (1898).

[70] *Ber.*, **29**, 1940 (1896).

[71] Manchot and Kampschulte, *Ber.*, **40**, 2891 (1907), have ascertained that while silver foil is not at all sensitive at ordinary temperatures, it becomes much more so at 220° to 240° C. For metallic mercury they found the temperature at which action was strongest to be 170° C.

[72] *Ber.*, **35**, 1324 (1902).

[73] *Ber.*, **39**, 2555 (1906).

[74] *J. Chem. Soc.*, **97**, 868 (1910).

[75] *Amer. Chem. J.*, **39**, 96 (1908).

Nitrogen peroxide and hydrogen peroxide, on the other hand, both reduce it instantly. To identify ozone in gases that contain at the same time nitrogen peroxide and hydrogen peroxide it is only necessary to draw the gases through a solution of potassium permanganate; the nitrogen peroxide and hydrogen peroxide will not pass through, while the ozone will, and can then be detected with potassium iodide and starch.

To detect nitrogen peroxide in the presence of ozone and hydrogen peroxide they took advantage of the fact that both ozone and hydrogen peroxide are decomposed when passed through a tube containing powdered manganese dioxide. Nitrogen peroxide passes through unchanged. Its presence can be shown by passing the gas, after it has gone over the manganese dioxide, into a very dilute solution of potassium permanganate. If the latter is decolorized, nitrogen peroxide was present. A still more delicate test for nitrogen peroxide is to pass the gas, which may contain ozone and hydrogen dioxide, directly into pure caustic soda, made from metallic sodium and nitrite-free distilled water, and then to test the caustic soda solution for nitrites by the well-known sulphanilic acid and α-naphthylamine method.

Hydrogen dioxide can be identified in the presence of both ozone and nitrogen peroxide by passing the gas mixture into a solution of potassium ferricyanide and ferric chloride. The yellow brown solution becomes green and then blue as more hydrogen dioxide passes in. This formation of Prussian blue is characteristic of hydrogen dioxide and is not produced by either ozone or nitrogen peroxide.

Determination of Ozone.—The quantitative determination of ozone in air, etc., is usually carried out by passing the gas through a solution of potassium iodide and titrating the iodine set free. Treadwell and Anneler[76] recommend this method, the ozonized oxygen being caused to act upon a neutral solution of potassium iodide,

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[76] *Z. anorg. Chem.,* **48**, 86 (1905).

$$2\,KI + O_3 + H_2O = 2\,KOH + 2\,I + O_2.$$

The liberated iodine is titrated with 0.1 *N* sodium thiosulphate after first acidifying the solution with dilute sulphuric acid.

$$1\text{ cc. }0.1\,N\ Na_2S_2O_3 = 0.0024\text{ gram }O_3.$$

An acid solution of potassium iodide may not be employed because hydrogen dioxide is then formed and this sets free a further amount of iodine.

$$4\,O_3 + 10\,HI + H_2O = 10\,I + 3\,O_2 + H_2O_2 + 5\,H_2O.$$

The gas sample is collected and measured in a bulb of the form shown in Fig. 69, which is a slight modification of that proposed by Treadwell. The bulb, *B*, has a capacity of from 300 cc. to 400 cc. and its volume is accurately determined by weighing it empty and then filled with water, applying correction for temperature.[77] The carefully ground slip-joint of glass, *A*, serves to connect the bulb with the apparatus from which the ozonized air is to be drawn. Rubber or cork connections may not be used because both are attacked by ozone.

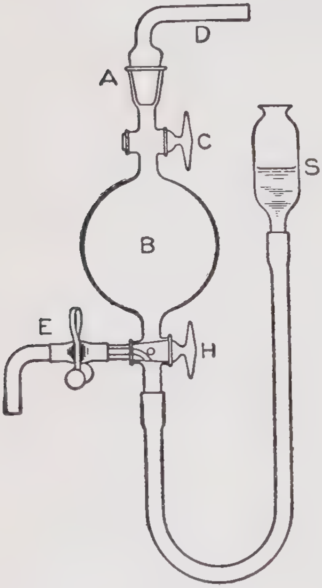

FIG. 69

The bulb is filled with distilled water, and the gas sample is drawn in through *A* by opening both stopcocks and allowing the water to flow out. The lower stopcock *H* is then closed and a few seconds later the upper stopcock *C* is closed. The inlet tube *D* is now removed and the stopcock *C* is opened for an instant to bring the gas to atmospheric pressure. The barometric pressure and the temperature of the room are read and recorded.

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[77] Treadwell-Hall, *Analytical Chemistry*, Vol. II (1911), p. 678.

The tube below *H* is connected by a piece of rubber tubing with the level-bulb *S* which is then filled with a 2 *N* solution of potassium iodide. Air in the rubber tube is driven out through the end opening of the tail-stopper *H*, and the stopper is then turned and from 20 cc. to 30 cc. of the solution is forced into the bulb. *H* is now closed and the rubber tube is taken off.

The bulb is vigorously shaken and allowed to stand for about half an hour, at the end of which time the absorption of ozone will be complete. The solution in the bulb is then run out into an Erlenmeyer flask, the bulb being rinsed with a small volume of the solution of potassium iodide and then finally with distilled water. The solution is acidified with dilute sulphuric acid and the free iodine is titrated with a 0.1 *N* solution of sodium thiosulphate. In computing the per cent of ozone in the gas mixture, the volume v of the gas sample in the bulb is first corrected to the volume v_0 that it would occupy under standard conditions by means of the formula given on page 32. If n represents the number of cubic centimeters of 0.1 *N* sodium thiosulphate used in the titration of the free iodine, then

$$\text{per cent by volume of ozone} = \frac{112 \times n}{v_0}$$

Treadwell and Anneler do not discuss the possibility of interference by nitrogen peroxide or hydrogen peroxide in their method for the determination of ozone nor do they describe any procedure for the removal of these gases. The ozone can be freed from these two gases by passing the mixture through a tube filled with chromic acid and then through an acid solution of potassium permanganate.[78]

The determination of ozone by means of potassium iodide has also been used by Lechner,[79] Czako,[80] Hayhurst and Pring,[81]

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[78] Bamberger and Trautzl, *Z. anal Chem.*, **64**, 9 (1924).
[79] *Z. Elektrochem.*, **17**, 412 (1911).
[80] *J. Gasbel.*, **55**, 768 (1912).
[81] *J. Chem. Soc.*, **97**, 868 (1910).

Pring,[82] Reynolds,[83] Bamberger and Trautzl,[84] and McDonnell.[85] Rothmund and Burgstaller[86] showed that in the determination of ozone and hydrogen peroxide, potassium iodide is untrustworthy on account of secondary reactions, but they pointed out that satisfactory results could be obtained by substituting potassium bromide in acid solution for the iodide, and then adding potassium iodide and titrating the liberated iodine.

Usher and Rao[87] made a thorough study of the determination of ozone and oxides of nitrogen in the atmosphere, and they found that the methods based on the use of potassium iodide are untrustworthy. The method of Rothmund and Burgstaller is unsuited for ozone in exceedingly small concentrations, and in the method of Hayhurst and Pring, modified by Pring, it is doubtful if complete absorption is obtained. In addition to the objections offered to this method by Rothmund and Burgstaller, they state that: (1) "The liberated iodine is appreciably volatile in the current of air, even when fairly concentrated potassium iodide is used; (2) when iodate is formed, the reaction between the iodic and hydriodic acids which occurs when the liquid is acidified is very slow at great dilutions; (3) any nitrous acid present is reduced to nitric oxide, which then combines with dissolved oxygen and furnishes more iodine; (4) solutions of potassium iodide are unstable in the presence of air, even in the dark." While the first three difficulties might be surmounted, the fourth is bound to occur. Baskerville and Crozier[88] have proposed the substitution of cadmium potassium iodide for potassium iodide. Usher and Rao do not think that this will eliminate these errors and they further object to the method of Keiser and McMaster because ozone will not pass unchanged through a solution of potassium permanganate unless both nitrogen peroxide and hydrogen peroxide are absent.

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[82] *Chem. News,* **109,** 73 (1914).
[83] *Nature,* **112,** 396 (1923).
[84] *Loc. cit.*
[85] *Ind. Eng. Chem.,* **18,** 135 (1926).
[86] *Monatsh.,* **34,** 75 (1913).
[87] *J. Chem. Soc.,* **111,** 799 (1917).
[88] *J. Amer. Chem. Soc.,* **34,** 1332 (1912).

Usher and Rao recommend a method which depends upon the reaction between ozone and alkali nitrite in aqueous solution. This takes place quantitatively according to the following equation:

$$O_3 + NaNO_2 = O_2 + NaNO_3$$

Two samples of the gas mixture are collected in 7-liter stopped bottles, Fig. 70. The bottles have glass stoppers which must fit accurately and be free from grease. They are thoroughly cleaned, washed with distilled water, and afterwards left for several days full of ozonized air to remove all traces of oxidizable matter.

The bottle *A* is first filled completely with pure water, which must be free from dissolved impurities, especially nitrous acid, and a rubber stopper is then inserted in the neck. This stopper carries two tubes, of which one, *B*, is of capillary bore and passes to the bottom of the bottle to admit the gas mixture. The other, *C*, is about 30 cm. long and 3 mm. bore, and projects only 1 or 2 mm. inside the stopper. This tube is provided with a stopcock and serves as an exit for the water. Outside the stopper the tube *B* is sealed (only sealed glass junctions are permissible) to the tube or tubes containing the chromic acid and manganese dioxide.

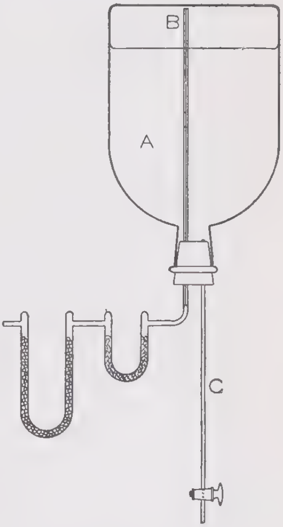

Fig. 70

The tube containing chromic acid has a bore of one cm.

and is filled with glass beads coated with purified chromic acid. The glass beads should occupy 30 cm. of the tube. The chromic acid is prepared by precipitating barium chromate, washing it thoroughly, and digesting with dilute sulphuric acid that is free from nitric acid. The solution of chromic acid is treated with sufficient solution of barium hydroxide to remove any sulphuric acid, and is then evaporated on a water bath until it becomes pasty. The glass beads are stirred into it, and are then introduced into the tube and dried in a current of air at 100°.

The manganese dioxide is mixed with asbestos wool that has been thoroughly washed and then ignited, and the mixture is packed into a tube which need be only one-half the length of the tube for chromic acid. The manganese dioxide should be free from alkali and manganous oxide, for otherwise it may take up small quantities of nitrogen peroxide.

On inverting the whole apparatus and opening the stopcock, the bottle fills with the gas mixture, the volume of which is equal to the water that escapes. The tube *B* is extended to the bottom of the bottle to avoid bubbling the gas through the water, which might dissolve some of the ozone and oxides of nitrogen. The samples are collected at the rate of about one liter per minute.

One sample is admitted through two tubes containing respectively chromic acid and powdered manganese dioxide, and the other through a tube containing chromic acid only. When the samples are collected, the rubber stoppers are withdrawn and are immediately replaced by glass ones. A 0.000025 *N* solution of sodium nitrite is prepared by dissolving the salt in in *N* solution of sodium hydroxide instead of in water. 25 cc. of this solution and 100 cc. of pure water are then introduced into each bottle. The glass stoppers are secured and the bottles are shaken for at least half an hour on a shaking machine. The contents of each is then made up to 250 cc., and 50 cc. of the solution is mixed with 5 cc. of the Griess-Ilosvay reagent (see p. 221) in a small stoppered flask which is kept in a water bath at 75° for ten minutes. 50 cc. of a standard solution of sodium nitrate (0.0000025 *N*) is treated in exactly the same manner. The strengths of the solutions are then measured in a Duboscq colorimeter. The first sample contains only nitrogen peroxide, as the ozone and hydrogen peroxide have been destroyed. The increase in nitrite content is equivalent to the nitrogen peroxide absorbed. The second sample contains ozone and nitrogen peroxide, and the difference between the quantities of nitrite in the two bottles is equivalent to the ozone.

The volume concentration of ozone will be 1 in

$$1/0.007\ (\mathrm{r/V} - \mathrm{r'/V'})$$

of air if the nitrite solutions are of the concentrations given, in which

V = cc. of air collected through chromic acid,

r and r′ = ratio of length of column of standard solution to that of treated solution,

V′ = cc. of air collected through chromic acid and manganese dioxide.

It is, of course, possible to determine hydrogen peroxide by collecting a third untreated sample, but the results would probably be unreliable due to the presence of impurities.

The presence of traces of ammonia, sulphur dioxide, or hydrogen sulphide does not interfere, as all of these gases are completely absorbed by the chromic acid. Chlorine or hydrogen chloride would make the determination of nitrogen peroxide impossible, but would not affect that of ozone.

Krueger and Moeller[89] employ an optical method for the determination of ozone based upon its absorption within the wave-lengths 200 to 300 $\mu\mu$.

HYDROGEN

Properties of Hydrogen.—Specific gravity (air = 1), 0.06965; density at 0°, 760 mm., 0.08987 gram per liter; critical temperature, —239.9°; critical pressure, 12.8 atmospheres; melting point, —259.1°; boiling point, —252.7°.

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[89] *Phys. Zeit.*, **13**, 729 (1912).

According to Winkler,[90] one volume of water absorbs at

0°, 0.02148 vol. hydrogen
5°, 0.02044 “
10°, 0.01955 “
15°, 0.01883 “
20°, 0.01819 “
25°, 0.01754 “

Detection of Hydrogen.—For the detection of hydrogen Phillips[91] recommends the use of dry palladious chloride which reacts with hydrogen with the formation of hydrogen chloride that then causes precipitation of silver chloride when the issuing gases are passed through a solution of silver nitrate. Since, however, palladious chloride is reduced by the olefines and by carbon monoxide the method is applicable to the detection of hydrogen only in such gas mixtures as do not contain these constituents. Zenghelis[92] has described a method that may be used for the detection of hydrogen in the presence of such hydrocarbons as methane, ethylene and acetylene. It consists in passing the gas mixture through a solution of sodium hydroxide and then through a tube fitted with a tip of platinum foil or platinum wire gauze. The foil or gauze should be carefully ignited before the test is made. This delivery tube is immersed in a few cubic centimeters of a warm solution of sodium molybdate contained in a test tube. The reagent is prepared by dissolving one gram of molybdenum trioxide in dilute sodium hydroxide, adding dilute hydrochloric acid in slight excess and diluting to 200 cc. with water. When molecular hydrogen passes through the delivery tube it is occluded by the platinum and in this condition immediately reduces the ammonium molybdate solution, imparting to the latter an intense blue color. If the amount of hydrogen is very small or if the molybdenum solution is cold, the color is a light greenish blue. Palladium is to be preferred to platinum in testing for hydrogen by this method, but the latter metal gives quite satisfactory results unless there is only a trace of hydrogen in the gas mixture. Arsine, phosphine and carbon monoxide will cause the reduction of the molybdenum solution and consequently these three gases must be removed before the test for hydrogen is made.

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[90] *Ber.*, **24**, 89 (1891); *Z. phys. chem.*, **9**, 171 (1892); see also Timofejeff, *Z. phys. Chem.*, **6**, 141 (1890).

[91] *Amer. Chem. J.*, **16**, 259 (1894).

[92] *Z. anal. Chem.*, **49**, 729 (1910).

Pereira [93] detects hydrogen by means of its reducing action (production of a blue coloration) on solutions of phosphomolybdic acid and sodium tungstate in the presence of palladium chloride as a catalyst; a precipitate of reduced palladium is also formed.

Determination of Hydrogen by Absorption.—Hempel [94] devised a method for the separation of hydrogen from ethylene, nitrogen, and gases of the paraffin series, in which the hydrogen, without being mixed with oxygen, is directly absorbed by palladium-black at a temperature of about 100°. The palladium-black is first rendered active by superficially oxidizing it by heating it to redness on the lid of a platinum crucible and slowly raising the crucible lid out of the flame. About four grams of this palladium-black is placed in a U-tube which is made of soft glass tubing. This tube has an internal diameter of 4 mm. and is 10 cm. high. To the upper ends of the U-tube are connected two bent capillary tubes. The one is connected with a gas pipette that contains water, and that is used simply to render possible the passage of the gas back and forth through the palladium-black. The other capillary tube is joined to the burette that contains the gas mixture in which free hydrogen is to be determined. Gases other than hydrogen, nitrogen, ethylene, and methane and its homologues must previously be removed by absorption. There is now brought up under the U-tube a beaker containing water at a temperature of about 100°. The point at which the water stands in the capillary of the pipette is noted, the pinchcock at the top of the burette is then opened and the gas mixture passed three times back and forth through the palladium tube by raising and lowering the level-tube. The beaker of hot water is now replaced by one containing water of the temperature of the room and the gas residue is twice passed back and forth through this tube to cool it. The gas is then drawn back into the burette until the water stands at the original point in the capillary of the pipette. The pinchcock is then closed and the residual gas volume in the burette is measured. The difference between the measurements made before and after the absorption is equal to the hydrogen in the gas mixture plus the volume of the oxygen in the air that was originally inclosed in the U-tube when the apparatus was put together.

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[93] *J. Amer. Chem. Soc. Abstr.*, **7**, 3284 (1913).
[94] *Ber.*, **12**, 636 (1879).

This volume of oxygen in the U-tube may accurately be determined once and for all in the following manner. Somewhat more than 100 cc. of air is drawn into a phosphorus pipette (Fig. 38) and allowed to stand until the oxygen has been removed and the fumes of phosphorus pentoxide have been absorbed. The pipette is connected with a gas burette and the nitrogen in the pipette is passed over into the burette and is measured. The pipette is now connected with one end of the freshly filled palladium tube which itself is immersed in a beaker of water of the temperature of the room. The other end of the U-tube is connected with the burette that contains the nitrogen. The level-tube of the burette is then raised and the nitrogen is driven over into the pipette until the confining liquid reaches the top of the burette. The pinchcock is then closed and the gas is allowed to stand in the phosphorus pipette for about three minutes. The gas is then drawn back into the burette and again passed over into the pipette. The residual nitrogen is then drawn back into the burette and its volume is read. The difference between this and the first reading gives the volume of oxygen that was originally in the palladium tube. The palladium-black must be regenerated from time to time by heating it on the lid of a platinum crucible in the manner above described.

The correct determination of hydrogen by this method is impossible in the presence of carbon monoxide, hydrogen chloride, and some other constituents, and for that reason its use in technical gas analysis is quite restricted.

Hydrogen may also be absorbed from a gas mixture by a fresh, warm, one per cent solution of palladious chloride in the manner described by Campbell and Hart,[95] provided that carbon dioxide, unsaturated hydrocarbons, oxygen, and carbon monoxide have previously been removed.

A method devised by Paal and Hartmann[96] for the volumetric determination of hydrogen is based upon the absorption of hydrogen by a solution of colloidal palladium with sodium protalbinate as a protective colloid. To avoid the necessity of oxidizing the palladium hydride after each absorption, they make use of the fact that hydrogen that has been absorbed by colloidal palladium is able rapidly to reduce organic nitro-compounds such as picric acid.

$$C_6H_2(NO_2)_3\ OH + 18\ H = C_6H_2(NH_2)_3\ OH + 6\ H_2O.$$

Consequently when sodium picrate is added in excess to the solution of the absorbent, the solution will rapidly and quantitatively absorb a large volume of hydrogen gas.

The authors prepare the reagent by dissolving two grams of sodium protalbinate in 50 cc. of water, adding sodium hydroxide in slight excess and then slowly adding 1.6 grams of palladium chloride (= 1 gram Pd) previously dissolved in 25 cc. of water. A reddish brown liquid results which remains clear. To this is added hydrazine hydrate drop by drop. Reduction takes place at once. The solution is allowed to stand for three hours and is then placed in a dialyzer and dialyzed against water until the outer water shows no further test for hydrazine hydrate or sodium chloride. The resulting solution is concentrated at a temperature of 68° to 70° and is then evaporated to dryness over concentrated sulphuric acid in a vacuum. Black, glistening plates result which are soluble in water without leaving a residue. For the absorption of hydrogen, the authors dissolve 2.74 grams of sodium picrate and 2.44 grams of 61.33 per cent colloidal palladium in water and dilute the solution to 130 cc. The reagent may be used in a Hempel simple gas pipette. Analyses made with this absorbent show that hydrogen is completely removed from a gas sample in from 10 to 30 minutes and that hydrogen may quantitatively be separated from nitrogen and saturated gaseous hydrocarbons. If oxygen is present with the hydrogen in the gas mixture, the oxygen should first be removed by means of alkaline pyrogallol or other suitable absorbent because of the fact that colloidal palladium will cause oxygen and hydrogen to unite. Carbon monoxide is not absorbed by the reagent, but the gas seems to retard the absorption of hydrogen by colloidal palladium. For this reason the authors recommend that carbon monoxide be first removed by ammoniacal cuprous chloride and that the hydrogen in the residue be then absorbed by the palladium solution.

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[95] *Amer. Chem. J.*, **18**, 294 (1896).
[96] *Ber.*, **43**, 243 (1910).

Brunck has made a careful examination of the method of Paal and Hartmann with a view to ascertaining whether it is adapted to technical practice.[97] He finds that the procedure gives very satisfactory results and states that he regards it as even more accurate than the combustion method for the determination of hydrogen. Brunck employs a Hempel gas burette with water as the confining liquid and a Hempel simple absorption pipette for solid and liquid reagents (see page 63), for holding the absorbent. The removal of the hydrogen is more rapid if the pipette is shaken or if it is filled with small glass balls of from 5 to 7 mm. diameter. The size of these glass balls should be such that when the pipette is filled with them it it will still be able to hold from

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[97] *Chem. Ztg.*, **34**, 1313 (1910).

80 to 90 cc. of gas. The absorbent is prepared by dissolving two grams of colloidal palladium in water and adding 5 grams of picric acid that has been neutralized with sodium hydroxide, and diluting the whole to from 100 to 110 cc. This amount of the reagent has a theoretical absorbing power of 4369 cc. of hydrogen measured under standard conditions. Relatively small amounts of hydrogen, 10 to 20 cc., are absorbed in about 5 minutes; somewhat larger amounts in about 10 minutes. When, however, the gas mixture contains 50 per cent or more of hydrogen, the gas should be passed over into the pipette and allowed to stand for 5 minutes, then drawn back into the burette so that the glass balls in the pipette again become moistened with the absorbent, and then passed back again into the pipette. This should be continued until no further diminution of gas volume is noted. The removal of hydrogen from 100 cc. of a gas mixture containing a high per cent of this gas takes from 20 to 30 minutes. This method is naturally best applicable to the determination of hydrogen in the presence of nitrogen or of methane, or of both of these gases. A series of analyses of a mixture of hydrogen and nitrogen shows that the determination of hydrogen is accurate to within 0.1 cc. which falls well within the limits of experimental error when the sample is not greater than 100 cc. and the analysis is made over water.

The high cost of the reagent would constitute a serious objection to its employment in technical practice were it not easily possible to regenerate it. This may be done[98] as follows: The reagent is transferred from the gas pipette to a flask and the pipette is rinsed with water which is added to the liquid in the flask. Very dilute sulphuric acid is added drop by drop to the solution so long as a precipitate results. A large excess of sulphuric acid is to be avoided because it might cause the colloidal palladium to change to palladium sulphate through action of atmospheric oxygen. The precipitate which contains palladium, free protalbinic acid and unused picric acid, is washed with water which, while it may dissolve some of the acids, carries no palladium into solution. The precipitate is then suspended in a small amount of water and is dissolved by adding sodium hydroxide drop by drop. Fresh sodium picrate is then added, and the solution diluted with water to its original volume of about 100 cc. It is now again ready for use.

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[98] Brunck, *Chem. Ztg.*, **34**, 1332 (1910).

Hempel[99] states that the solution of colloidal palladium foams very strongly and that this necessitates waiting a considerable length of time after the absorption of hydrogen is complete until the foam has disappeared and the gas residue can be transferred to the burette for measurement. He cites experiments carried on by Petschek which show that the absorbing liquid prepared according to the method of Paal and Hartmann slowly loses its absorbing power even when it stands in the dark. For this reason Hempel recommends that the reagent be used over mercury in an absorption pipette and that small quantities of the freshly prepared absorbing liquid be employed for the analyses.

Burrell and Oberfell[100] found that the solution obtained by Brunck's method of preparation contains more sodium picrate and therefore has a longer life. By passing the gas back and forth into an Orsat pipette, it required from six to thirty minutes to completely remove the hydrogen, the time depending upon the amount of hydrogen present. They add that the removal would probably be more rapid if the gas samples were shaken with the reagent in a Hempel pipette. They consider this method preferable to the use of palladium sponge or palladium asbestos, and they state that the liquid does not lose its absorbing power.

Bossard and Fischeli[101] have suggested the use of a solution of sodium oleate containing nickel in suspension, for the gas analytical absorption of hydrogen. Anderson and

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[99] *Z. angew. Chem.*, **25**, 1841 (1912).
[100] *Ind. Eng. Chem.*, **6**, 992 (1914).
[101] *Z. angew. Chem.*, **28**, 365 (1915).

Katz[102] investigated this method and found that there are certain objections which make it unsatisfactory.

Hofmann[103] recommends the absorption of hydrogen by means of a pipette containing clay tubes which are covered with platinum and palladium, and are immersed in a solution containing sodium chlorate, sodium bicarbonate, and osmic acid. Sulphur, vapor of phosphorus, phosphine, and ammonia act as contact poisons, and carbon monoxide must be completely removed by means of mercuric chromate. The full efficiency of the reagent is not obtained until 200 to 300 cc. of hydrogen have been absorbed.

Determination of Hydrogen by Explosion.—Hydrogen may be determined by mixing the gas with not more than four times its volume[104] of pure oxygen, exploding the mixture and measuring the contraction of the gas volume. The gas mixture may be exploded over mercury in a eudiometer such as Bunsen employed, or the explosion pipette described on page 138 may be used. The volume of hydrogen that was present is equal to two-thirds of the observed contraction

$$2\ H_2 + O_2 = 2\ H_2O.$$

If air is employed instead of oxygen, it should be borne in mind that a mixture of hydrogen and air that contains less than 10 per cent or more than 63 per cent of hydrogen is not explosive[105] and that the most accurate results will be obtained when the ratio of the volume of the gas that does not enter into the explosion to that of the hydrogen and oxygen uniting is about 4 to 1. The determination of hydrogen by explosion with oxygen or air is not well suited to technical gas analysis because the reaction is so violent as to necessitate the use of only a small volume of hydrogen with consequent decrease in the accuracy of the results. Moreover, as Misteli points out,[106] small amounts of hydrogen escape combustion in the determination of the gas by explosion. Furthermore when nitrogen is present there is possibility of error through the formation of oxides of nitrogen.

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[102] *Ind. Eng. Chem.*, **10**, 23 (1918).
[103] *Ber.*, **48**, 1585 (1915); **49**, 1650 (1916).
[104] Bunsen, *Gasometrische Methoden*, 2d ed., p. 119.
[105] Teclu, *J. prakt. Chem.*, **75**, 212 (1907).
[106] *J. Gasbel.*, **48**, 802 (1905).

Determination of Hydrogen with Combustion Pipette.—Hydrogen may be determined with a high degree of accuracy by the combustion method described by Dennis and Hopkins[107] (see p. 143). In this method the hydrogen may first be introduced into the combustion pipette (see Fig. 66) and then burned with a mixture of equal parts of oxygen and air, or pure oxygen may be introduced into the pipette and the hydrogen be then passed in. Either procedure gives equally accurate results. In the first form of manipulation a sample (about 100 cc.) of the hydrogen under examination is measured off in a burette and is then passed over into the combustion pipette. A mixture of about equal parts of oxygen and air containing an amount of oxygen more than sufficient for the combustion of the hydrogen is measured off in the burette, and the burette and pipette are then connected by a bent glass capillary tube in the usual manner (see Fig. 67). The platinum spiral is heated to dull redness by means of an electric current, and the mixture of air and oxygen is slowly passed over from the burette into the pipette. During the combustion the current should be regulated by means of the rheostat so that the spiral is at no time heated beyond dull redness. The combustion of the hydrogen is complete almost as soon as sufficient oxygen has been introduced. When nearly all of the mixture of air and oxygen is passed into the pipette, the pinchcock at the top of the burette is closed and the spiral is kept at dull redness for sixty seconds. The current is then turned off, the pipette is allowed to cool and the residual gas is passed back into the burette and measured. In this form of the method the hydrogen is burned with a mixture of oxygen and air because if pure oxygen were used, the contraction in the gas volume in the pipette before an excess of oxygen is introduced would cause the mercury in the pipette to rise and submerge the platinum spiral. The results of a series of determinations of hydrogen made by this method are given in the following table:

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[107] *J. Am. Chem. Soc.*, **21**, 398 (1899).

TABLE XI

	I cc.	II cc.	III cc.	IV cc.	V cc.	VI cc.	VII cc.	VIII cc.
Hydrogen taken	99.6	100.0	98.6	99.8	99.4	95.35	97.5	51.15
Oxygen and air added	99.6	99.95	99.9	100.0	99.1	96.6	99.75	48.95
Total	199.2	199.95	198.5	199.8	198.5	191.95	197.25	100.10
Residue after combustion	50.0	50.1	50.8	50.55	49.7	49.1	51.2	23.4
Contraction	149.2	149.85	147.7	149.25	148.8	142.85	146.05	76.7
Equivalent to hydrogen	99.47	99.9	98.47	99.5	99.3	95.23	97.37	51.13
	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
Hydrogen found	**99.9**	**99.9**	**99.9**	**99.7**	**99.9**	**99.9**	**99.9**	**100.0**

In the other style of manipulation a measured amount (about 100 cc.) of oxygen is passed into the combustion pipette, the sample of hydrogen under analysis (about 100 cc.) is measured off in the burette, the burette and pipette are connected, the spiral is brought to dull redness and the hydrogen is slowly passed into the pipette until the following confining liquid reaches the connecting capillary. In either manner of manipulation, the confining liquid, water or mercury, should not be driven further than this because if it were to come in contact with the hot part of the pipette directly over the platinum spiral the glass would probably crack. To insure the complete transferral of the hydrogen from the burette into the pipette the level-tube of the burette is now lowered and about 25 cc. of gas is drawn back into it from the pipette. This is then driven over again into the pipette and the procedure is once more repeated. The spiral is kept at dull redness for sixty seconds longer, the pipette is then allowed to cool and the gas is passed back into the burette and measured.

Carter[108] states that the combustion of hydrogen with oxygen is not theoretically complete even at atmospheric pressure because of the dissociation of the water vapor formed. The addition of nitrogen diminishes the degree of dissociation.

Hydrogen may also be determined by combustion over a heated platinum wire as described on page 150.

The Fractional Combustion of Hydrogen.—In the analysis of those mixtures of gases that most commonly occur in technical practice, the determination of the majority of the constituents may be accomplished by the absorption of the gases by liquid reagents or by solid reagents immersed in liquids. This method is, however, not applicable to the determination of the gases of the paraffin series nor is it always possible or feasible to remove hydrogen by means of a liquid absorbent. In gas mixtures or gas residues that contain hydrogen and only one member of the paraffin series, both gases may satisfactorily be determined by burning the gases simultaneously in the combustion pipette shown in Fig. 66, measuring the contraction, and ascertaining the volume of carbon dioxide that has been formed. The analysis of such a mixture of combustible gases by the explosion method (see p. 138) is not as accurate as that by the combustion method just referred to. Particularly is this true of the simultaneous determination of hydrogen and methane in gas residues that contain large amounts of these two gases, for in such case only a small portion of the combustible residue can safely be exploded and consequently any experimental error is multiplied five- to eight-fold when the results are calculated for the whole of the gas residue. Moreover, if two or more hydrocarbons of the same group are present with the hydrogen, the gases cannot be determined by any combustion or explosion method in which all of the combustible gases are simultaneously burned (see p. 126). For these reasons a satisfactory method for the fractional combustion of mixtures of hydrogen and hydrocarbons of the paraffin group, a method by means of which the hydrogen gas alone may be burned without oxidation of the hydrocarbons, has long been sought and many different procedures have been suggested.

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[108] *J. Gasbel.*, **56**, 545, 570 (1913).

The fractional combustion of hydrogen can be carried out most satisfactorily by the use of copper oxide (see p. 157), but the combustion with palladium asbestos (p. 151), palladium black (p. 155), or a platinum capillary tube (p. 149) may also be used.

Hurwitz[109] has described an apparatus for the determination of hydrogen in gas mixtures which depends upon the velocity of sound in the gas mixture, referred to air as the standard.

NITROGEN

Properties of Nitrogen.—Specific gravity (air = 1), 0.96737; density at 0°, 760 mm., 1.2504 grams per liter; critical temperature, —147.1°; critical pressure, 33.5 atmospheres; melting point, —209.8°; boiling point, —195.8°.

Nitrogen is but slightly soluble in water, one volume of water absorbing, according to Fox,[110] at 760 mm. pressure and

at 0°, 0.02359 vol. atm. nitrogen
“ 5°, 0.02103 “ “ “
“ 10°, 0.01895 “ “ “
“ 15°, 0.01731 “ “ “
“ 20°, 0.01598 “ “ “
“ 25°, 0.01489 “ “ “
“ 30°, 0.01398 “ “ “

Absorption of Nitrogen.—In the analysis of gas mixtures the residue that cannot be determined by the usual absorption methods or by combustion was earlier regarded as consisting wholly of nitrogen and is still commonly reported as such. From the researches of Rayleigh and Ramsay we now know that this residue frequently contains, in addition to nitrogen, one or more of the gases of the argon group, which comprises argon, neon, krypton, xenon and helium. In the earlier work in this field, nitrogen was separated from the gases by passing the gas mixture over hot magnesium, lithium, or a mixture of magnesium and calcium oxide, any of which agents unite with the nitrogen but do not affect the gases of the argon group.

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[109] *Z. tech. Physik.*, **6**, 113 (1925).
[110] *Farad. Trans.* **5**, 68 (1909).

To obtain information as to the relative efficiencies of these various absorption agents, Hempel placed the different substances in hard-glass tubes, exhausted these tubes of air, and then introduced an excess of nitrogen. The tubes were then heated to bright redness, the nitrogen was pumped out and measured, and the amount of that gas which had been held back by each absorbent was thus determined.

From these experiments it appeared that, of the substances tried, the best absorbent for nitrogen is a mixture of one part by weight of finely powdered magnesium with five parts by weight of freshly ignited lime in pieces about as large as poppy seeds, and 0.25 part by weight of metallic sodium. The magnesium should be intimately mixed with the ignited lime, but it is sufficient to add the sodium in the form of a number of pieces each about half as large as a pea. The layer of oxide covering the metallic sodium should first be removed, and the metal should be added to the mixture just before using. One gram of this mixture absorbed on one hour's contact about 52 cc. of nitrogen.

Magnesium and lime react to form metallic calcium. Since the above experiments were made, metallic calcium has come upon the market, and this may now be used directly for the removal of the nitrogen, instead of being formed within the apparatus by the interaction of magnesium and lime. Metallic calcium energetically combines with nitrogen forming calcium nitride, Ca_3N_2.

The researches of Fischer[111] have demonstrated that calcium carbide may be employed for the absorption of nitrogen and also for the simultaneous removal of oxygen.

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[111] *Ber.*, **41**, 2017 (1908); see also Natus, *Gas World*, **60**, 35.

To remove nitrogen from a mixture of this gas with the gases of the argon group, the gas mixture, after having been freed from other constituents, may be driven backward and forward by means of mercury through a heated tube containing one or another of the above absorbents. Constant raising and lowering of the mercury level-bulbs is, however, a tedious procedure, and for this reason, if any appreciable amount of nitrogen is to be removed, it will be found convenient to employ the Travers[112] modification of the automatic device described by Collie.[113] By means of this apparatus the gases can automatically be driven through the absorption apparatus in a continuous current. Fig. 71 shows an arrangement of the apparatus substantially in the form recommended by Travers except that the bulb reservoir is here replaced by a two-neck Wolff bottle with a tubulure at the bottom, and an iron tube containing metallic calcium is used in place of a glass tube filled with magnesium turnings. A small Wolff bottle, *A*, that has two necks and a tubulure at the bottom, is connected with the level-bulb *B* by means of enamelled rubber tubing. Into the two necks of the Wolff bottle are inserted, by means of rubber stoppers, two glass tubes, one with a two-way stopcock and the other with a single stopcock. The tube *D* is bent as shown in the figure and is provided with a small bulb *S* for catching any mercury that may be carried up through *D*. The apparatus may be connected with a mercury air pump through the side-arm *T*. The end of *D* is connected by rubber tubing, securely wired in place, with the tube *E* of Jena glass containing partially reduced copper oxide, and the tube *F* containing soda lime and phosphorus pentoxide. The tube *G* is connected with the tube *H* which is of iron, and is about 1.5 meter long and about 2 cm. inner diameter. *H* is filled with pieces of metallic calcium, or, if this not available, with the mixture of magnesium, freshly ignited lime and metallic sodium recommended by

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[112] Travers, *Experimental Study of Gases,* p. 101.
[113] *J. Chem. Soc.,* **55,** 110 (1889).

Hempel. *E* and *H* rest in combustion furnaces. The metallic copper is used for the removal of any oxygen that might be present in the gas mixture. The copper oxide serves to oxidize hydrogen and carbon monoxide. Hydrogen may result from the action of water vapor upon the metallic calcium.

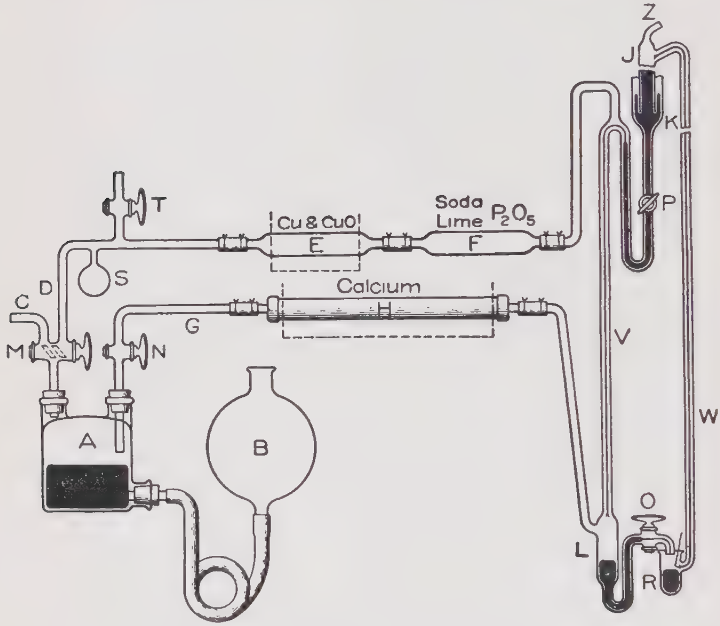

Fig. 71

The carbon monoxide may diffuse into the apparatus through the hot iron tube. To avoid this last mentioned difficulty Fischer and Hähnel[114] suggest that the iron tube be surrounded by sheet copper 2 mm. thick.

The further ends of *F* and *H* are connected with the Collie apparatus in the manner shown in the figure. To prepare the apparatus for use the level-bulb *B* is raised and mercury is forced up to the stopcock *N* and through the stopcock *M* to the end of the branch tube *C*, and *M* and *N* are then closed. *C* is now connected with the gasometer containing the gas mixture to be treated, *M* is opened, *B* is lowered and the gas is drawn into the bottle *A*. *M* is then closed. The stopcocks *O* and *P* are also closed, the tubes *F* and *H* are heated and the apparatus is exhausted through *T* by means of a mercury pump until gases cease to be given off. *T* is then closed and *M* is carefully turned to such a position that *A* communicates with *D; N* is next opened and then the stopcock *P*. Mercury from the reservoir *K* now drops down through the capillary tube *V* carrying with it gas into *L* and forcing the gas through *H*. The stopcock *O* is turned so that mercury flows from *L* into *R* in a steady stream. *R* is provided with a side capillary tube *W* which connects with the tube *J*, this latter tube dipping into the mercury in the reservoir *K*. The upper end of the tube *J* is connected through *Z* with a water suction pump. A twisted piece of rusty iron wire is inserted in the lower end of the capillary tube *W* to prevent the mercury that flows into *R* from *L* from completely closing the capillary. This results in the mercury being drawn up through *W* in a series of fine drops which fall into the reservoir *K*. In this manner the gases are continuously forced through *H* and *A* and back through *D, E* and *F*, and the process will run for hours without attention if the iron wire was properly adjusted and the flow of mercury was carefully regulated at the beginning of the experiment.

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[114] *Ber.*, **43**, 1436 (1910).

Further amounts of the original gas mixture may be introduced through *C* when desired. After all of the gases except those of the argon group have been removed, the gas mixture remaining in the apparatus may be pumped out through *T* by means of a Töpler pump, and collected as described on page 8, or the stopcock *N* may be closed, and such of the gas residue as is in *A* may be driven out through *C* into a suitable container by raising the level-bulb *B* and turning the stopcock *M* into the proper position.

A method and apparatus for the determination of the nitrogen that is evolved from metals which are fused in a vacuum has recently been described by Jordan and Eckman.[115] They pass the evolved gases into a tube containing vapor of calcium. The nitrogen is absorbed by the calcium vapor and is finally determined in the resulting calcium nitride by dissolving the contents of the tube in hydrochloric acid, adding a concentrated solution of nitrogen-free sodium hydroxide, and distilling the ammonia into a standard solution of sulphuric acid.

For the removal of large amounts of nitrogen from the air Fischer and Ringe[116] have employed commercial calcium carbide. This substance reacts at high temperatures with nitrogen with the formation of calcium cyanamide and the separation of carbon, according to the equation,

$$CaC_2 + N_2 = N \equiv C - N = Ca + C.$$

They find that this reaction does not reverse at a temperature of about 800°, and that both nitrogen and oxygen may quantitatively be removed by this means.

Le Blanc and Eschmann[117] have shown that this reaction is quantitative from left to right up to about 1150°. The calcium carbide is placed in a thick-walled iron cylinder of sufficient size to hold about seven kilograms of the carbide. The operation is conducted in a manner essentially similar to that already here described, except that the circulating device differs from that employed by Collie and Travers.

Natus[118] recommends the direct determination of nitrogen by absorption with finely powdered calcium carbide containing one-tenth of its weight of fused calcium chloride. A known weight of this mixture, which has been previously heated in a current of hydrogen, is placed in a porcelain boat within a porcelain tube, and is then heated to 900° to 1000°. The nitrogen is absorbed by passing the gas back and forth twice through the tube by means of gas burettes at the ends of the porcelain tube. The nitrogen content of the product is then determined by Wilfarth's modification [119] of the Kjeldahl method.

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[115] *U. S. Bureau of Standards, Scientific Paper* No. 563 (1927).
[116] *Ber.*, **41**, 2017 (1908).
[117] *Z. Elecktrochem.*, **17**, 20 (1911).
[118] *Z. anal. Chem.*, **52**, 265 (1913).

With the apparatus devised by Henrich and Eichhorn,[120] free nitrogen can quantitatively be removed from gaseous mixtures by the action of an electric spark in the presence of oxygen, a solution of sodium hydroxide being used for the absorption of the oxides of nitrogen that are formed.

TABLE XII

GASES OF THE ARGON GROUP

	Helium†	Neon	Argon	Krypton	Xenon
Atomic weight	4.002	20.18	39.94	82.9	130.2
Density	0.1785	0.8999	1.7836	3.708	5.851
Melting point	−272.2	−248.67	−189.2	−169	−140
Boiling point	−268.9	−245.9	−185.7	−151.8	−109.1
Critical temperature	−267.9	−228.7	−122.4	− 62.6	− 16.6
Critical pressure	2.26	26.9	48.0	54.2	58.2
Per cent by volume in air	0.0005	0.00123	0.933	0.5×10^{-5}	0.6×10^{-6}

† Paneth and Peters, *Z. phys. Chem.*, **134**, 353 (1928).

After the removal of nitrogen from the air by the methods given under Nitrogen, the gases of the argon group will remain. Detailed information concerning the separation of these gases from one another will be found in Travers, *Study of Gases* (1901), Friend, *Textbook of Inorganic Chemistry*, Vol. I (1914), and Gmelin-Meyer, *Handbuch der Anorganischen Chemie*, Vol. I (1926).

NITROUS OXIDE (N_2O)

Properties of Nitrous Oxide.—Specific gravity (air = 1), 1.5208; density at 0°, 760 mm., 1.9777; critical temperature, 36.5°; critical pressure, 71.7 atmospheres; melting-point, — 102.4°; boiling point, — 88.7°; specific gravity of liquid gas at 0° (water at 4°), 0.9105.

[119] Treadwell-Hall, *Analytical Chemistry*, Vol. II, p. 63 (1911).

[120] *Z. angew. Chem.*, **25**, 468 (1912).

Nitrous oxide is quite soluble in water, one volume of water dissolving at 760 mm. pressure and

0°, 1.3052 vol. N_2O
5°, 1.0954 " "
10°, 0.9196 " "
15°, 0.7778 " "
20°, 0.6700 " "
25°, 0.5962 " "

One volume of alcohol dissolves at 20° 3.0253 volumes N_2O.

Detection of Nitrous Oxide.—No satisfactory method has yet been devised for the detection of small amounts of nitrous oxide. Lunge has proposed[121] that the gas mixture under examination be passed through absolute alcohol in which nitrous oxide is quite readily soluble while the other gases with which it is usually associated are not appreciably dissolved. The method serves merely to concentrate the nitrous oxide and cannot be regarded as a means of its identification.

The procedure suggested by Hempel[122] is similar in character, the gases being condensed by means of liquid air and then fractionally distilled. This yields a residue rich in nitrous oxide, in which the presence of the gas is indicated by the increase in volume that results when it is dissociated by mixing with it oxyhydrogen gas and exploding the mixture.

Determination of Nitrous Oxide.—For the determination of nitrous oxide a variety of methods has been proposed. Wagner[123] passes the gas over a hot mixture of chromium oxide and sodium carbonate. The nitrous oxide is reduced to nitrogen, while any nitric oxide that may be present is unaffected. The amount of nitrous oxide may be calculated from the volume of nitrogen set fee, or from the amount of sodium chromate that is formed.

Von Dumreicher[124] burns the gas with hydrogen in a eudiometer. Water and nitrogen are formed, and the latter is measured. Hempel recommends[125] this method but adds oxyhydrogen gas also. He uses his explosion pipette for the combustion and finds that the results are satisfactory if the volume of hydrogen is two to three times that of the nitrous oxide and if, further, such an amount of oxyhydrogen gas is added as will give 26 to 64 volumes of combustible gas to every 100 volumes of incombustible gas. The decrease in volume is equal to the volume of nitrous oxide.

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[121] *Ber.*, **14**, 2188 (1881).
[122] *Z. Elektrochem.*, **12**, 600 (1906).
[123] *Z. anal. Chem.*, **21**, 374 (1882).
[124] *Kais. Akad. d. Wissen. Wien.*, **82**, 560 (1881).

$$N_2O + H_2 = N_2 + H_2O$$

Von Knorre and Arndt[126] pass a mixture of nitrous oxide and hydrogen through a hot Drehschmidt capillary tube (see p. 149) and obtain satisfactory results. They also find that this method gives approximately accurate results in the analysis of a mixture of nitrous oxide and nitric oxide. An excess of hydrogen is added to the gas mixture and the gases are then *slowly* passed through a Drehschmidt capillary tube heated to bright redness.

$$2\,NO + 2\,H_2 = N_2 + 2\,H_2O$$

Too rapid passage of the gas will cause the formation of some ammonia from the nitric oxide.

$$2\,NO + 5\,H_2 = 2\,NH_3 + 2\,H_2O$$

The volumes of the two oxides of nitrogen in the gas mixture may be calculated from the contraction. If $V =$ the volume of the gas mixture, and $C =$ the contraction, then

$$V = \text{vol. } N_2O + \text{vol. } NO,$$
$$C = \text{vol. } N_2O + 1\tfrac{1}{2} \text{ vol. } NO,$$

and from the foregoing

$$\text{vol. } NO = 2\ (C - V).$$

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[125] *Ber.*, **15**, 903 (1882); see also *Z. Elecktrochem.*, **12**, 600 (1906).

[126] *Ber.*, **32**, 2136 (1899); **33**, 30 (1900).

If nitrogen also is present, then

$$\begin{aligned} V &= \text{vol. } N_2O + \text{vol. } NO + \text{vol. } N_2 \\ C &= \text{vol. } N_2O + 1\tfrac{1}{2} \text{ vol. } NO \\ \text{vol. } H_2 &= \text{vol. } N_2O + \text{vol. } NO, \end{aligned}$$

from which it follows that

$$\begin{aligned} \text{vol. } N_2O &= 3 \text{ vol. } H_2 - 2\ C \\ \text{vol. } NO &= 2\ (C - \text{vol. } H_2) \\ \text{vol. } N_2 &= V - \text{vol. } H_2. \end{aligned}$$

According to Pollak[127] it is not satisfactory to determine nitrous oxide by combustion with hydrogen in a Drehschmidt capillary tube, because if carbon dioxide is present it takes part to some extent in the combustion,

$$CO_2 + H_2 = H_2O + CO.$$

He recommends freeing the gas from oxygen by moist phosphorus and then mixing the residue with carbon monoxide and passing this gas mixture through a hot Drehschmidt capillary tube. The carbon dioxide that is formed is determined by the ordinary method, its volume being equal to the volume of nitrous oxide present,

$$N_2O + CO = CO_2 + N_2.$$

Baskerville and Stevenson[128] state that none of the well-known methods are reliable for an accurate determination of nitrous oxide in a gaseous mixture in which it is the principle constituent. They recommend the determination of nitrous oxide by the following indirect method: A measured volume of the gas mixture is passed through a tower containing solid sodium hydroxide and a long tube filled with calcium chloride to remove acid gases and moisture. The gas is then passed over ignited copper gauze which has previously been reduced in a current of hydrogen. The gas sample is followed by hydrogen until the copper oxide that has been formed in the

[127] Treadwell-Hall, *Analytical Chemistry,* Vol. II., p. 804 (1911).
[128] *Ind. Eng. Chem.,* **3**, 579 (1911).

first reaction is completely reduced, and the water that is formed in this last stage is collected in drying tubes. They are then weighed and the amount of nitrous oxide in the gas sample is calculated from the weight of water that has been formed.

The method cannot be used for the determination of nitrous oxide in gas mixtures that contain other oxides of nitrogen or oxygen, or other gases that would be decomposed by the metallic copper with the formation of copper oxide, unless the amounts of these gases are determined and the water that results from them is subtracted from the total amount of water found. Baskerville and Stevenson find that these gases are not present in the samples of commercial compressed nitrous oxide that they analyzed.

Burrell and Jones[129] have analyzed the commercial compressed nitrous oxide by fractional distillation at low temperatures. According to Richardson and Woodhouse,[130] nitrous oxide can accurately be determined in mixtures of this gas with carbon dioxide by explosion with hydrogen. The carbon dioxide is absorbed by a strong solution of potassium hydroxide which does not dissolve the nitrous oxide. Satisfactory combustion is obtained if the gases are thoroughly mixed and a small amount of water is introduced into the explosion pipette.

Milligan[131] has found that nitrous oxide can accurately be determined in a mixture of nitrogen peroxide, nitric oxide, nitrous oxide, and nitrogen. The gases are conveyed through the apparatus with pure carbon dioxide. The nitrogen peroxide and nitric oxide are absorbed in two wash-bottles, one containing concentrated sulphuric acid, and the other a mixture of concentrated sulphuric and nitric acid. The carbon dioxide is absorbed by a 20 per cent solution of sodium hydroxide. The nitrous oxide and nitrogen are determined by slow combustion with an excess of hydrogen, using a red-hot platinum spiral (see p. 143).

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[129] *Ind. Eng. Chem.,* **8,** 735 (1916).
[130] *J. Amer. Chem. Soc.,* **45,** 2638 (1923).
[131] *J. Phys. Chem.,* **28,** 544 (1924).

NITRIC OXIDE (NO)

Properties of Nitric Oxide.—Specific gravity (air = 1), 1.0367; density at 0°, 760 mm., 1.3402 grams per liter; critical temperature, —96°; critical pressure, 64 atmospheres; melting point —160.9°; boiling point, —150.2°.

Nitric oxide is but slightly soluble in water, one volume of water dissolving, according to Winkler,[132] at 760 mm. pressure and at

0°,	0.07381	vol.
5°,	0.06461	"
10°,	0.05709	"
15°,	0.05147	"
20°,	0.04706	"
25°,	0.04323	"
30°,	0.04004	"

Nitric oxide cannot be kept over water without undergoing change. Nitrous acid is formed together with some hyponitrous acid which breaks down partly into nitrous oxide and partly into ammonia. The latter then reacts with the nitrous acid and liberates nitrogen, which accounts for the presence of this gas in quite large amount in nitric oxide that has been stored over water for a considerable length of time.

Nitric oxide is absorbed by solutions of ferrous salts, potassium permanganate, potassium dichromate, and alkaline sodium sulphite. It is also taken up by concentrated sulphuric acid, one cc. of this acid of 1.84 specific gravity absorbing 0.035 cc. of nitric oxide. If the acid has a specific gravity of 1.5, one cc. of it will absorb 0.017 cc. of the gas.

Hydrogen peroxide reacts with nitric oxide to form nitric acid and water.

Detection of Nitric Oxide.—A delicate method for the detection of nitric oxide consists in passing the gas, mixed with air, through a dilute solution of the hydroxide of either sodium or potassium and adding Griess's reagent. The reactions that take place in the absorption are, according to Le Blanc,[133] as follows:

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[132] *Ber.*, **34**, 1408 (1901).

$$2\,NO + O_2 \longrightarrow 2\,NO_2,$$
$$NO + NO_2 \longrightarrow N_2O_3,$$
$$NO_2 + \text{absorbent} \longrightarrow \text{nitrate and nitrite},$$
$$N_2O_3 + \text{absorbent} \longrightarrow \text{nitrite}.$$

The nitrite that has thus been formed in the absorbent is detected by first adding acetic acid to the sodium hydroxide or potassium hydroxide until the solution has a faint acid reaction and then adding Griess's reagent as improved by Ilosvay[134] and Lunge.[135] The reagent in this modified form is prepared as follows: 0.5 gram of sulphanilic acid is dissolved in 150 cc. of dilute acetic acid. 0.1 gram of solid α-naphthylamine is boiled with 20 cc. of water, the colorless solution is poured off from the violet residue and to the solution 150 cc. of dilute acetic acid is added. The two solutions are then mixed and the reagent is kept in a tightly stoppered bottle.

Lunge states that the reagent is not at all affected by the light. This is contradicted by Reckleben, Lockemann and Eckardt[136] who state that even in diffused daylight the reagent soon takes on a yellowish-red color which renders the detection of small amounts of nitrous acid impossible. They find that if the solution is kept in the dark it remains completely clear and colorless for months.

In making the test the acidified solution of the absorbent is warmed to about 80° and about one-fifth of its volume of the Griess's reagent is added. If nitric oxide was present in the gas mixture, the solution turns red. The reaction is extremely delicate, one part of nitrous acid in one thousand million parts of the solution giving a distinct red coloration after one minute.

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[133] *Z. Elektrochem.*, **12**, 541 (1906).
[134] *Bull. soc. chim.* [3], **2**, 347 (1889).
[135] *Z. angew. Chem.*, 666 (1889).
[136] *Z. anal. Chem.*, **46**, 671 (1907).

Determination of Nitric Oxide.—Nitric oxide may quantitatively be determined by absorption of the gas with a solution of ferrous sulphate. The reagent contains one part by weight of the salt dissolved in two part by weight of water, and it is very slightly acidified with dilute sulphuric acid. It is used in a Hempel double pipette for liquid reagents. This reagent, however, tends to give up the absorbed nitric oxide to indifferent gases, and the method does not yield correct results when nitrous oxide is present with the nitric oxide.

It has been proposed [137] to determine nitric oxide by mixing it with hydrogen and burning the mixture in a Drehschmidt capillary tube (see under Nitrous Oxide). Moser, who has made a careful comparison of the various methods for the determination of this gas, states [138] that this method does not yield uniform results both because of the secondary reaction which causes the formation of ammonia and because of the porosity of red-hot platinum to gases.

According to Pollak [139] a mixture of nitric oxide and carbon monoxide can be burned by conducting the mixture through a Drehschmidt platinum capillary heated to bright redness. The combustion is quantitative only if the carbon dioxide that is formed is immediately removed with caustic potash. This is done by placing a few cubic centimeters of a solution of potassium hydroxide on the mercury in the pipette connected to the Drehschmidt tube. The reaction is

$$2\,NO + 2\,CO = 2\,CO_2 + N_2.$$

If at the same time considerable nitrous oxide is present, the combustion takes place quantitatively even without the removal of the carbon dioxide and the contraction is one-half the volume of the nitric oxide.

The absorption of nitric oxide by sodium sulphite is original with Divers,[140] who, however, gives no details concerning the preparation of this solution further than to say that it is "a strong solution of either sodium or potassium sulphite to which a little alkali hydroxide has been added." He states that it "quickly absorbs every trace of nitric oxide, which it fixes in the form of hyponitrososulphate, $Na_2N_2O_2SO_3$."

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[137] Knorre and Arndt, *Ber.*, **32**, 2136 (1899).
[138] *Z. anal. Chem.*, **50**, 401 (1911).
[139] Treadwell-Hall, *Analytical Chemistry*, Vol. II, 4th ed., p. 804.

Moser finds that this reagent is not superior to ferrous sulphate and that the absorption by sodium sulphite takes place quite slowly and is complete only after long shaking.

Terres[141] determines nitric oxide by oxidizing it to nitrogen peroxide, absorbing that gas in potassium hydroxide, reducing with Devarda's[142] alloy, distilling and titrating.

A titrimetric method for the determination of nitric oxide is based upon the reaction between the gas and an acidulated solution of potassium permanganate.

$$10\ NO + 6\ KMnO_4 + 9\ H_2SO_4 = 3\ K_2SO_4 + 6\ MnSO_4 + 10\ HNO_3 + 4\ H_2O.$$

The reaction was first examined by Terreil[143] who found that nitric oxide is completely oxidized to nitric acid by a neutral or an acidified solution of potassium permanganate, while nitrous oxide is not attacked. Lunge[144] ascertained that the speed of reaction between nitric oxide and a 0.1 *N* solution of potassium permanganate is so slight that complete absorption of the gas is attained only when an apparatus that brings about prolonged and intimate contact between the gas and absorbent is employed. He recommends for this purpose the ten-bulb tube shown on page 389, but better results will undoubtedly follow the employment of a Friedrichs spiral gas washing bottle, page 119. Before beginning the determination the air in the apparatus must be displaced by carbon dioxide because of the reaction between nitric oxide and oxygen. To avoid this operation and also to obtain more complete absorption, Moser[145] suggests that the gas mixture be passed into a spiral absorption bulb that is made entirely of glass and that is figured in his article.

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[140] *J. Chem. Soc.*, **75**, 82 (1899).
[141] *J. Gasbel.*, **57**, 700 (1914).
[142] Treadwell-Hall, *Analytical Chemistry*, Vol. I, p. 34 (1916).
[143] *Compt. rend.*, **63**, 970 (1866).
[144] *Z. angew. Chem.*, 567 (1890).

The potassium permanganate is approximately decinormal in strength and to every 100 cc. of the solution is added from 30 to 50 cc. of 2 *N* sulphuric acid. An excess of a standardized solution of ferrous sulphate is added to the potassium permanganate and the excess of ferrous sulphate is titrated back with potassium permanganate.

The results by this method even when the Moser absorption bulb is employed are somewhat lower than those obtained by absorption with ferrous sulphate, which Moser ascribes to the reaction between the nitric oxide and the oxygen dissolved in the solution of potassium permanganate.

Geake and Squire[146] have used this method for the analysis of nitrous gases. Burdick[147] absorbs the gas in an excess of 0.1 *N* alkali, and titrates one portion with acid and another portion with potassium permanganate to determine both nitric oxide and nitrogen peroxide.

Milligan[148] found that when nitric oxide is absorbed by a neutral or acidified 0.3 *N* solution of potassium permanganate, satisfactory results could not be obtained because of the precipitation of oxides of manganese, which, however, can be prevented by the addition of phosphoric acid.

Schönbein[149] found that when nitric oxide was brought into contact with an excess of hydrogen peroxide the gas is oxidized to nitric acid:

$$2\,NO + 3\,H_2O_2 = 2\,HNO_3 + 2\,H_2O$$

The applicability of this reaction to the determination of nitric oxide has been studied by Davis,[150] by Wilfarth[151] and by Lunge.[152] Lunge discarded the method because his experiments indicated that the removal of nitric oxide by hydrogen peroxide either in acid or in alkaline solution was not complete. Moser[153] found that this criticism is correct when the method is carried out in the manner described by Wilfarth and by Lunge, but he states that with the absorption bulb that he devised it is possible to obtain complete oxidation of nitric oxide in from six to twelve minutes. He employs as absorbent a three per cent solution of hydrogen peroxide in a definite volume of which (about 110 cc.) the free acid is first determined by titration with a standardized solution of potassium hydroxide, using a one per cent solution of phenolphthalein as indicator. The reagent is then brought into the absorption bulb, the gas is passed in from a gas burette, and the gas and hydrogen peroxide are shaken together for several minutes. The absorbent is then transferred to a beaker and the nitric acid that has been formed is titrated with potassium hydroxide. If acid or alkaline gases are present in the gas mixture under examination, they must first be removed by passing the mixture through suitable absorption apparatus. Under such conditions, however, the determination of the nitric oxide with potassium permanganate is preferable to that with hydrogen peroxide.

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[145] *Loc. cit.*
[146] *J. Soc. Chem. Ind.*, **38**, 367 (1919).
[147] *Ind. Eng. Chem.*, **14**, 308 (1922).
[148] *J. Phys. Chem.*, **28**, 547 (1924).
[149] *J. prakt. Chem.*, **81**, 265 (1860).
[150] *Chem. News*, **41**, 188 (1880).
[151] *Z. anal. Chem.*, **23**, 587 (1884).
[152] *Z. angew. Chem.*, 568 (1890).

The method of Ilosvay and Lunge for the detection of nitrites may also be employed for the determination of nitric oxide. A measured amount of air is drawn through a solution of sodium hydroxide or potassium hydroxide, and the color that results when Greiss's reagent[154] is added under the conditions above prescribed is compared with the color yielded by a standard nitrite solution. For approximate work the standard solution may be prepared by dissolving a weighed amount of either potassium nitrite or sodium nitrite in water. If greater accuracy is desired the standard nitrite solution may be prepared by precipitating a solution of silver nitrate with sodium nitrite, recrystallizing the silver nitrite twice from hot water and then adding to its solution in hot water sodium chloride, and removing the precipitated silver chloride by filtration.

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[153] *Loc. cit.*

[154] Treadwell-Hall, *Analytical Chemistry*, Vol. II, p. 306 (1928).

Allison, Parker and Jones[155] have used this method for determining small quantities of oxides of nitrogen other than nitrous oxide, which result from the firing of explosives. With a 250 cc. sample they were able to determine as low as 10 parts of oxides of nitrogen per million parts of air with an accuracy of about 5 parts per million. Francis and Parsons[156] object to this method on account of the incomplete oxidation by means of hydrogen peroxide in alkaline solution. They collect the sample in a bottle and oxidize the nitric oxide by adding 7 cc. of acidulated hydrogen peroxide and allowing it to stand for three hours with frequent shaking. The acid is neutralized with potassium hydroxide, and the solution then evaporated to dryness. The residue is cooled, moistened with 2 cc. of phenol disulphonic acid reagent,[157] diluted, made ammoniacal with 15 cc. of 7.5 *N* ammonium hydroxide, and the color is then compared with a standard. The method is applicable to the determination of nitric oxide in a concentration of over one part per million, and it may be used for smaller quantities if the nitric oxide is first condensed by means of liquid air.

Baudisch and Klinger[158] determine nitric oxide by passing air into the gas mixture that stands in contact with solid potassium hydroxide. The nitric oxide is oxidized to N_2O_3 which is quickly absorbed by the alkali; no nitrogen peroxide is formed.

The reactions are

$$(1) \qquad 4\,NO + O_2 = 2\,N_2O_3$$

$$(2) \qquad 2\,N_2O_3 + 4\,KOH = 4\,KNO_2 + 2\,H_2O \qquad \text{or}$$

$$4\,NO + O_2 + 4\,KOH = 4\,KNO_2 + 2\,H_2O.$$

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[155] *U. S. Bureau of Mines, Tech. Paper* 249 (1921).

[156] *Analyst*, **50**, 262 (1925).

[157] Am. Pub. Health Assoc., *Standard Methods of Water Analysis*, (1920), p. 23.

[158] *Ber.*, **45**, 3231 (1912).

Therefore four-fifths of the observed contraction corresponds to the nitric oxide present. There must be an excess of oxygen present at the end of the process to prevent the formation of nitrogen peroxide. The nitric oxide, air, and potassium hydroxide must be perfectly dry[159] and the caustic potash frequently renewed. The nitric oxide is dried by passing it through concentrated sulphuric acid which also removes traces of N_2O_3. The air should first be freed from carbon dioxide.

Koehler and Marqueyrol[160] state that mono-ethylamine is much better for the absorption of the N_2O_3 formed as above than potassium hydroxide which will absorb other gases. The absorption of carbon dioxide by mono-ethylamine is so small that it may be disregarded. The gas sample and 0.6 cc. of mono-ethylamine are introduced into a eudiometer standing in a mercury trough, and oxygen is admitted, a bubble at a time, until after the absorption of the nitric oxide an excess of about 5 cc. of oxygen remains. The excess of oxygen may be removed by an alkaline solution of pyrogallol.

Milligan[161] found that the most satisfactory reagent for the absorption of nitric oxide is concentrated (95 per cent) sulphuric acid, to every 100 cc. of which is added 2 cc. of concentrated nitric acid.[162] This mixture absorbs nitric oxide with the formation of nitrosylsulphuric acid, according to the reaction

$$HNO_3 + 2\ NO + 3\ H_2SO_4 = 3\ NOHSO_4 + 2\ H_2O$$

and the trivalent nitrogen in the acid, from which the nitric oxide is calculated, is afterward determined by titration with potassium permanganate. The nitric oxide which a given volume of this reagent is called upon to absorb should always be considerably less than the amount equivalent to the nitric acid present.

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[159] Klinger, *Ber.*, **46**, 1744 (1913).

[160] *Bull. soc. chim.* [4], **13**, 69 (1913).

[161] *J. Phys. Chem.*, **28**, 548 (1924).

[162] See also Sanfourche, *Bull. soc. chim.*, **31**, 1248 (1922); *Compt. rend.*, **175**, 469 (1922).

NITROGEN PEROXIDE (NO_2)

Properties of Nitrogen Peroxide.—Specific gravity (NO_2), 1.5906. Weight of one liter (NO_2), 2.0563 grams. The molecule of nitrogen peroxide is considered to have the formula N_2O_4 at temperatures below — 11° and to dissociate into NO_2 as the temperature rises. At the average temperature of the laboratory the gas will contain both the simpler molecule NO_2 and the polymer N_2O_4.

When brought into contact with water, nitrogen peroxide forms nitric acid, nitrous acid and nitric oxide, according to the equations

$$O_2N \cdot NO_2 + H_2O = HO \cdot NO_2 + HO \cdot NO,$$

$$3\,O_2N \cdot NO_2 + 2\,H_2O = 4\,HO \cdot NO_2 + 2\,NO.$$

When nitrogen peroxide is passed through a dilute solution of sodium hydroxide, oxygen or air being absent, sodium nitrite and nitrate are formed [163] in the proportions shown in the first equation above. If, however, oxygen or atmospheric air is present with the nitrogen peroxide, some of the nitrite is oxidized to nitrate. The gas is rapidly absorbed by concentrated sulphuric acid (1.7 to 1.8 sp. gr.), nitrosylsulphuric acid and nitric acid being formed.

$$O_2N \cdot NO_2 + SO_2\,(OH)_2 = SO\,(OH)\,(ONO) + HO \cdot NO_2$$

Nitrogen peroxide may be detected by absorbing the gas in a dilute solution of sodium hydroxide, acidifying this with acetic acid and adding Griess's reagent. (See under Nitric Oxide.)

The absorption by sulphuric acid forms the best method for the determination [164] of nitrogen peroxide. If the sulphuric acid is concentrated, both products are stable and have low vapor pressures. The nitrous nitrogen (*i.e.*, nitrogen in the nitrosylsulphuric acid) may be determined by titration with potassium permanganate, and the total nitrogen may be calculated from measurement of the volume of nitric oxide evolved when a given volume of acid is shaken with mercury in a nitrometer. When the sulphuric acid has absorbed pure nitrogen peroxide, the nitrous nitrogen is one-half of the total nitrogen.

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[163] Lunge and Berl, *Z. angew. Chem.*, **19**, 857 (1906).

[164] Lunge, *Ber.*, **15**, 488 (1882); Lunge and Berl, *Z. angew. Chem.*, **19**, 809, 858 (1906); **20**, 1714 (1907); Sanfourche, *Compt. rend.*, **175**, 469 (1922); *Bull. soc. chim.*, **31**, 1248 (1922); Milligan, *J. Phys. Chem.*, **28**, 545 (1924).

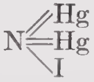
AMMONIA (NH_3)

Properties of Ammonia.—Specific gravity, 0.5971; density at 0°, 760 mm., 0.7708 gram per liter; critical temperature, 131°; critical pressure, 113 atmospheres; melting point, — 77.7°; boiling point, — 33.1°. One volume of water absorbs at a pressure of 760 mm.,

at 0°,	1176	vol.
8°,	947	“
13°,	837	“
16°,	775	“
20°,	702	“
24°,	639	“
28°,	586	“

Alcohol and ether also absorb considerable quantities of the gas.

Detection of Ammonia.—Ammonia may be detected when present in fairly large amounts by means of litmus paper or turmeric paper. A more sensitive reagent for the detection of minute amounts of ammonia is Nessler's reagent which is an alkaline solution of potassium mercuric iodide, K_2HgI_4. When ammonia acts upon this solution, mercurammonium iodide



is formed. If the amount of ammonia is appreciable, the compound appears as a reddish brown precipitate. With smaller amounts of ammonia it imparts merely a yellow color to the solution. The reaction is very delicate; 0.05 mg. of ammonia in one liter of water can readily be detected.

Ammonia may be determined[165] by either one of the two following variations of procedure. A measured volume of the gas mixture is passed through a known amount of dilute acid of known strength, and the amount of acid neutralized by the ammonia is determined by titration of the excess of acid. To determine whether the amount of ammonia present is above or below a definite amount, a predetermined amount of gas is passed through the solution of acid and the occurrence or absence of a change of color of the indicator noted. In general, however, the latter method is neither so accurate nor so convenient as the titration of the excess of acid.

As an absorbing agent, 0.02 N sulphuric acid is to be preferred, although the strength may be varied for different conditions. The most satisfactory indicators for the titration are sodium alizarinsulphonate, cochineal, or paranitrophenol.

The Bureau of Standards has investigated four common forms of absorption apparatus, including the ordinary gas wash-bottle, and has found that the ammonia can be determined with sufficient accuracy for either official or commercial testing with any of the forms. If glass beads are used in the absorption apparatus, a test should be made to determine the amount of acid neutralized by the solution of the alkali from the beads. The method of washing the beads should also be tested to insure completeness of washing with a minimum amount of wash water.

If the amount of ammonia in the gas mixture is very small, as for example in atmospheric air, the ammonia may be absorbed by passing it through ammonia-free distilled water slightly acidified with sulphuric acid and then determining the ammonia colorimetrically with Nessler's reagent.

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[165] Edwards, *Ind. Eng. Chem.*, **6**, 468 (1914); *Bureau of Standards Tech. Paper* No. 34 (1914); *Circular* No. 48, p. 146 (1916).

CARBON DIOXIDE (CO_2)

Properties of Carbon Dioxide. — Specific gravity (air = 1), 1.5197; density at 0°, 760 mm., 1.9768 grams per liter; critical temperature, 31°; critical pressure, 73 atmospheres; melting point, — 57°; boiling point, — 79°. According to Bohr, one volume of water absorbs at 760 mm.,

at 0°,	1.713	vol.
5°,	1.424	"
10°,	1.194	"
15°,	1.019	"
20°,	0.874	"
25°,	0.759	"
30°,	0.665	"

One cc. of sulphuric acid (sp. gr. = 1.78) dissolves, at 14° C. and 816.4 mm. pressure, 1.16 cc. of carbon dioxide.

Carbon dioxide is readily absorbed by a solution of potassium hydroxide or of barium hydroxide.

Determination of Carbon Dioxide.—For the volumetric determination of the gas, a solution of one part of caustic potash or caustic soda in two parts of water is employed. For the rapid and approximate determination of carbon dioxide by means of this absorbent, the Honigmann gas burette may be used. Somewhat more accurate results, however, can be obtained with the Bunte gas burette.

The most satisfactory forms of absorbing apparatus for use in technical gas analysis are the spiral pipette described on p. 76 or the Hempel simple pipette for solid and liquid reagents (Fig. 38). With the latter, the cylindrical part *C* is first closely filled with very short rolls of iron wire gauze. The gauze has a mesh of 1 to 2 mm., and the rolls are from 1 to 2 cm. long and about 5 mm. thick. The high viscosity of the reagent causes it to cling to the wire gauze when the gas is passed into the pipette and, as a consequence, the absorption of the carbon dioxide is very rapid. The viscosity of the reagent serves also to protect the iron wire gauze from oxidation by any oxygen in the gas mixture. Unless the amount of carbon dioxide in a gas mixture is unusually high, it is quantitatively removed by simply passing the gas once into either pipette and allowing it to remain there for one minute.

This reagent also absorbs sulphur dioxide, hydrogen sulphide, and any other acid vapors which may be present. It may also absorb some hydrocarbon vapors, such as benzene, making the result for carbon dioxide slightly high. This effect may be avoided by using a more dilute solution (1:3) or, better, by freeing the gas mixture from ammonia by dilute acid and hydrogen sulphide by hydrated ferric oxide, and making a gravimetric or volumetric determination by absorbing the carbon dioxide in a soda-lime tube or with a standard solution of barium hydroxide (see Chap. XIX).

Lange[166] has described a method for the analysis of liquid carbon dioxide using a modified Winkler burette. Thiele and Deckert[167] later recommended a method for this analysis whereby the gases other than carbon dioxide may be determined. Special methods have also been described for the determination of carbon dioxide in the presence of chlorine.[168]

Special methods for the determination of small percentages of carbon dioxide such as are found, for example, in atmospheric air are described in Chapter XIX, and those for the automatic determination in flue gases in Chapter XV.

CARBON MONOXIDE (CO)

Properties of Carbon Monoxide.—Specific gravity (air = 1), 0.9673; density at 0°, 760 mm., 1.2504 grams per liter; critical temperature, —138.7°; critical pressure, 34.6 atmospheres; boiling point, —190°; melting point, —207°.

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[166] *J. Soc. Chem. Ind.*, **20**, 122 (1901).

[167] *Z. angew. Chem.*, **20**, 737 (1907).

[168] Thorne and Keane, *Technical Methods of Chemical Analysis*, Vol. I, p. 590 (1924).

According to Winkler[169] one volume of water absorbs at 760 mm. and at

0°,	0.03537 vol.
5°,	0.03149 "
10°,	0.02816 "
15°,	0.02543 "
20°,	0.02319 "
25°,	0.02142 "
30°,	0.01998 "

Detection of Carbon Monoxide by Blood Spectrum.—The most delicate and dependable method for the detection of carbon monoxide is that in which the gas is absorbed by a solution of blood and the resulting carbon monoxide hæmoglobin is detected by the spectroscope. When a dilute solution of pure blood is brought before the slit of the spectroscope, two absorption bands, lying between the Fraunhofer lines *D* and *E*, are seen (Fig. 72, spectra No. 1 and No. 2). If, now, a reducing agent, such as ammonium sulphide, is added to the blood solution, these two bands, which are due to the oxyhæmoglobin of the blood, disappear and are replaced by a single broad and weakly defined band (spectrum No. 4).

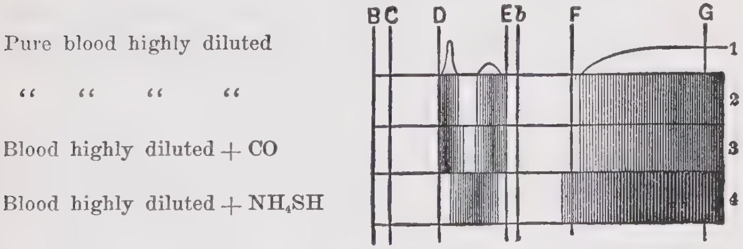
B
C
D
E
b
F
G
1
2
3
4
Pure blood highly diluted
" " " "
Blood highly diluted + CO
Blood highly diluted + NH₄SH

FIG. 72

When, however, carbon monoxide has previously been brought into contact with the blood solution, the two absorption bands due to carbon monoxide hæmoglobin (spectrum

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[169] *Ber.*, **34**, 1408 (1901).

No. 3) do not disappear when the reducing agent is added. Consequently the persistence of these two separate absorption bands is conclusive proof of the presence of carbon monoxide in the gas mixture under examination.

The solution of blood for use in this test is prepared by freeing a sample of blood from fibrin by beating it with a bundle of straws and then diluting the clear blood with an equal volome of a cold, saturated solution of borax. The addition of borax prevents putrefaction and does not change the spectroscopic properties of the blood, reduction and combination with oxygen and carbon monoxide taking place just as readily as if fresh blood or a solution of hæmoglobin were employed. The solution used in the absorption of carbon monoxide is prepared from the concentrated solution by mixing one cc. of the latter with 19 cc. of water. This gives a blood solution of the concentration 1 in 40. The absorption of carbon monoxide by this dilute blood solution may be effected by filling a 100 cc. bottle with water, emptying it in the room of which the air is to be tested for carbon monoxide, introducing 3 cc. of the dilute blood solution into the bottle, inserting the stopper in the bottle and then thoroughly shaking the bottle to bring the blood into contact with the inclosed gas. A more efficient absorption apparatus is that designed by Wolff[170] (Fig. 73). In preparing this apparatus for use a small wad of glass wool is inserted into *D* from above and gently pressed into place. The tube is then filled up to *F* with moderately fine, powdered glass. The grains of glass should be about as large as those

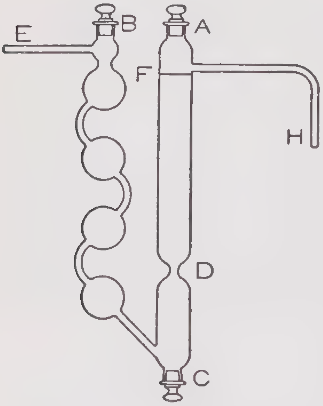

FIG. 73

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[170] *Correspondenzblatt des Vereins analytischer Chemiker*, **3**, 46, (1880).

of ordinary gunpowder and before its introduction into the tube the glass should be thoroughly cleansed by boiling it with hydrochloric acid, and washing it with distilled water. Two cc. of the dilute blood solution (1 in 40) is then introduced through *A* from a pipette. *A* is closed and by gently blowing into *H* the blood solution is caused to uniformly distribute itself throughout the column of powdered glass. The side tube *E* is now connected with the gas mixture (air) that is to be tested for carbon monoxide, and the gas is driven or drawn through the absorption tube, its volume being measured by a gas meter or other suitable device attached to *H*. To prevent the evaporation of the water from the blood solution in the absorption apparatus, it is advisable to insert between *E* and the source of gas a U-tube or wash bottle containing sufficient water to keep the entering air saturated with moisture. If only very small amounts of carbon monoxide are to be expected, a sample of air of about 10 liters should be passed through the absorption apparatus at a rate of about 3 liters per hour. If it is not convenient to set up the apparatus in or near the room whose atmosphere is to be tested, the sample may be collected in a 10 liter bottle by filling the bottle with water and emptying it in the room.

After the absorption of carbon monoxide by the blood solution has been accomplished in either of the two ways above described, the solution is transferred to a small test tube and examined with a spectroscope. If the Wolff absorption tube has been used, the blood solution is removed after the test by taking out the stoppers *A* and *C*, placing the test tube under *C*, and slowly dropping pure water upon the powdered glass. The liquid is collected in the test tube until the volume amounts to 3 cc. Since 2 cc. of the dilute blood solution (1 in 40) was originally used, the resulting 3 cc. of solution would now have a concentration of 1 in 60.

Any spectroscope of not too great dispersion may of course be employed for the examination of the blood spectrum, but a small direct vision spectroscope is quite as satisfactory for this purpose as a larger one. For checking the result of the spectroscopic examination, a second small test tube should be filled with the original blood solution, also diluted to 1 in 60, that has not been exposed to the action of the gas. One drop of a strong solution of ammonium sulphide is added to the contents of each tube, the tubes are corked and thoroughly shaken, and the spectra are examined after the tubes have stood for about half an hour. The presence of the two absorption bands shown in Fig. 72, spectrum No. 3, in the blood solution that has been exposed to the gas, and the absence of these bands in the solution of pure blood is conclusive proof of the presence of carbon monoxide in the air under examination. When the test is made in this manner the delicacy of the method is about 0.03 per cent by volume of carbon monoxide.

Kostin has found[171] that if the oxygen of the air is first removed, the delicacy of the blood test for carbon monoxide is greatly enhanced, and that under these conditions one part of the gas in forty thousand parts of air may be detected. The removal of oxygen may be effected by passing the air through 3 liters of a saturated solution of ferrous sulphate to which 1 liter of strong ammonium hydroxide has been added. The solution is placed in an aspirator bottle that is filled with iron wire gauze (*A*, Fig. 74). Four liters of this solution which contains much undissolved ferrous hydroxide is able to absorb the oxygen contained in 80 liters of air. Two such bottles are employed, the air under examination being first drawn into one and then driven into over the other, and passed backwards and forwards between the two aspirators until all oxygen has been removed. The residual gas is next forced from one aspirator into the other through one of the washing flasks *BB′* and the absorption apparatus *K* containing the blood solution. The washing flasks are charged with oxalic acid for the removal of any ammonia that may be given off from the material in the aspirator bottles.

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[171] *Arch. ges. Physiol.*, **83**, 572 (1901).

Ogier and Kohn-Abrest remove[172] oxygen by means of a solution of sodium hyposulphite, which is probably more rapid in its action and more convenient to handle than is the reagent used by Kostin.

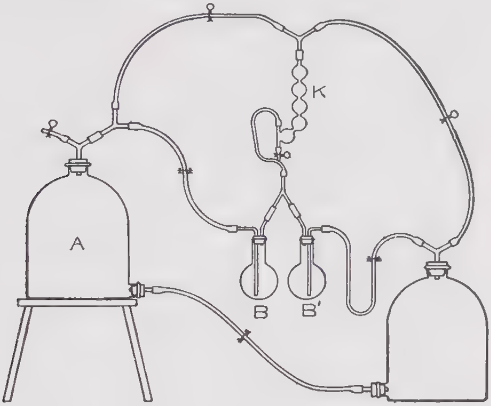

FIG. 74

Some investigators are of the opinion that the best method for detecting the presence of carbon monoxide in blood is that suggested by Kunkel. The blood is here diluted with 10 volumes of water and an equal volume of a 3 per cent tannin solution is then added. If the blood contains carbon monoxide, a reddish preciptate is formed, while with normal blood the precipitate is dark brown. These color reactions become especially distinct after five or six hours.

On the other hand, Doepner[173] finds that the spectroscopic detection of carbon monoxide in blood is fully as satisfactory as the best of the precipitation methods, and Florentin and Vandenberghe[174] and Nicloux[175] state that this is the most satisfactory test for carbon monoxide, because the iodine pentoxide method (see below) is not specific. The fresh beef blood is treated with one-tenth its volume of alcohol, added very slowly, to prevent fermentation and clotting. The oxygen is removed from the air by treatment with a solution containing 20 grams sodium hyposulphite, 20 cc. of a solution of sodium hydroxide (sp. gr. 1.33), and 80 to 100 cc. of water. 0.2 to 0.3 cc. of the blood is mixed with 18 cc. of water and 2 cc. of an ammoniacal solution of sodium hyposulphite (60 mg $Na_2S_2O_4$ and 20 cc. of 0.3 N NH_4OH), and the solution is examined with a spectroscope. The air is passed through the absorption tube at about 600 cc. per hour. To determine the quantity of carbon monoxide it is only necessary to ascertain how much air is required to make the absorption bands visible. By means of a slightly modified technique which is described in the later article, Nicloux found it possible to increase the sensitiveness of this test.

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[172] *Ann. chim. analyt. appl.*, **13**, 218 (1908).

[173] *Z. Medizinalbeamte*, **22**, 287 (1909).

[174] *Bull. soc. chim.*, [4], **29**, 316 (1921).

[175] *Bull. soc. chim.*, [4], **33**, 818 (1923); [4], **37**, 760 (1925); *Compt. rend.*, **180**, 1750 (1925).

Detection of Carbon Monoxide by Means of Iodine Pentoxide.—Iodine pentoxide and carbon monoxide react on each other with the liberation of free iodine and the formation of carbon dioxide.

$$I_2O_5 + 5\ CO = 2\ I + 5\ CO_2$$

De la Harpe and Reverdine[176] first utilized this reaction for the detection of carbon monoxide. More recently Levy and Pecoul[177] find that by passing the liberated iodine into chloroform, minute amounts of carbon monoxide in air can be detected. They state that one volume of carbon monoxide in 10,000 volumes of air will set free sufficient iodine to give to the chloroform an intense color. If acetylene is present in no greater proportion than 1: 10,000, it will cause no coloration of the chloroform, but larger amounts of acetylene should be removed before the test is made.

Hoover[178] gives a colorimetric method for the detection of carbon monoxide which is based upon the green color that is produced when carbon monoxide reacts with Hoolamite, which is a mixture of iodine pentoxide, fuming sulphuric acid, and pumice. This reagent will give positive indications for carbon monoxide in air in concentrations above 0.07 per cent.[179] Unsaturated hydrocarbons, gasoline vapor, hydrogen sulphide, arsine, hydrogen cyanide, and various complex organic compounds, especially those containing halogens or amino nitrogen, interfere, but they are removed if the gas mixture is first passed through fresh, activated charcoal. Hydrogen, methane, sulphur dioxide, nitrogen peroxide, ammonia, chlorine, and phosgene do not interfere with this test.

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[176] *Chem. Ztg.*, **12**, 1726 (1888).
[177] *Compt. rend.*, **142**, 162 (1906).
[178] *Ind. Eng. Chem.*, **13**, 770 (1921).

Teague[180] has also used the iodine pentoxide method for the detection of carbon monoxide, liquid air being employed to remove the interfering substances.

Rideal and Taylor[181] have described a recorder which depends upon the variation in conductivity of a standard solution of lime-water resulting from the absorption of the carbon dioxide that is formed by the oxidation of the carbon monoxide.

Other Methods of Detection.—Potane and Dronane[182] detect the presence of small quantities of carbon monoxide by passing the gas mixture through a dilute solution of palladium dichloride, whereupon metallic palladium is separated:

$$CO + PdCl_2 + H_2O = CO_2 + Pd + 2\ HCl.$$

Large quantities of carbon monoxide decolorize the solution and give it a grey color, but with only traces of carbon monoxide the solution is a light yellow. The metallic palladium is filtered off and the color of the solution is compared with the original solution. Wein[183] uses a 0.05 per cent solution of $Pd(NH_3)_2Cl_2$ and determines the carbon monoxide by the time that is necessary to produce the first visible precipitate.

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[179] Katz and Bloomfield, *Ind. Eng. Chem.*, **14**, 304 (1922).
[180] *Ind. Eng. Chem.*, **12**, 964 (1920).
[181] *Analyst*, **44**, 89 (1919).
[182] *Compt. rend.*, **126**, 938.
[183] *Glückauf*, **61**, 1623 (1925).

Nowicki[184] employs strips of paper moistened with a solution of palladium dichloride. The blackening of the paper indicates the presence of carbon monoxide. Brunck[185] also uses a solution of palladium chloride containing about one-half its volume of a 5 per cent solution of sodium acetate. The separated palladium is filtered off, dried, ignited in hydrogen, and weighed. This method cannot be used in the presence of hydrogen or unsaturated hydrocarbons because they also reduce palladium dichloride.

In a recent article, Katz, Reynolds, Frevert and Bloomfield[186] have described, with references to the previous development, a carbon monoxide detector and alarm which measures by means of thermocouples the increased temperature of the gases when the carbon monoxide and oxygen react in the presence of a catalyst. The recorder is not appreciably affected by the presence of other gases, and is sensitive to about 2 parts per million.

Hofmann[187] has used the retardation of the oxidation of hydrogen in a chlorate pipette (see p. 205) due to the presence of carbon monoxide, as a means of detecting the presence of small quantities of carbon monoxide.

Determination of Carbon Monoxide by Absorption.—For the absorption and volumetric determination of carbon monoxide, a hydrochloric acid or an ammoniacal solution of cuprous chloride is employed.

The hydrochloric acid solution of cuprous chloride may be prepared, according to Winkler, by adding a mixture of 86 grams of copper oxide and 17 grams of finely divided metallic copper to 1086 grams of hydrochloric acid (sp. gr. = 1.124), the mixture being slowly introduced and the acid frequently stirred. The copper powder is best prepared by the reduction of copper oxide with hydrogen. After this mixture has been added to the acid, a spiral of copper wire reaching from the bottom of the bottle up to its neck is inserted, and the bottle is closed with a soft rubber stopper. The solution is dark in the beginning, but upon standing it becomes wholly colorless. In contact with the air, however, it again turns dark brown, and some cupric chloride forms.

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[184] *Chem. Ztg.*, **35**, 1120 (1911).

[185] *Z. angew. Chem.*, **25**, 2479 (1912).

[186] *Bureau of Mines, Tech. Paper* No. 355 (1926).

[187] *Ber.*, **51**, 837 (1918).

Sandmeyer[188] treats 25 parts of crystallized copper sulphate and 12 parts of dry sodium chloride with 50 parts of water, and heats until the copper sulphate dissolves. Some sodium sulphate may separate out at this point, but it is not removed. To this solution 100 parts of concentrated hydrochloric acid and 13 parts of copper turnings are added, and the whole is boiled in a flask until decolorized.

Krauskopf and Purdy[189] prepare an acid solution of cuprous chloride by the reduction of cupric chloride with stannous chloride. Their solution contained 269 grams of cupric chloride, 616 cc. of concentrated hydrochloric acid (11.2 N), and 188 cc. of a saturated solution of stannous chloride per liter. The presence of stannic and stannous chlorides, even in relatively large amounts, does not impair the efficiency of the solution for the absorption of carbon monoxide. The authors give data to show that 200 cc. of this solution will quantitatively absorb about 365 cc. of carbon monoxide. The solution may be renewed, after being saturated with carbon monoxide, by heating to 60° to 70° for several hours on a water-bath under a reflux condenser.

In the Cornell laboratory it has been found that this method of preparation is much more satisfactory than that of either Winkler or Sandmeyer. Kropf[190] and Moser and Hanika[191] state that the addition of stannous chloride to an acid solution of cuprous chloride gives increased absorptive power. They find that the most suitable concentration for this solution is 16 to 18 parts of cuprous chloride, 24 to 27 parts of concentrated hydrochloric acid, and 60 to 55 parts of water, with the addition of 0.2 to 0.3 gram of stannous chloride ($SnCl_2 \cdot 2H_2O$).

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[188] *Ber.*, **17**, 1633 (1884).

[189] *Ind. Eng. Chem.*, **12**, 158 (1920).

[190] *Z. angew Chem.*, **35**, 451 (1922).

[191] *Z. anal. Chem.*, **67**, 448 (1926).

Czako[192] states that the acid cuprous chloride solution should be colorless. He makes the determination of carbon monoxide in illuminating gas in a Bunte burette. The gas should be treated with three successive portions of not more than 5 cc. each, for not more than two minutes each, to prevent the solubility of methane and benzene in this reagent.

The ammoniacal solution of cuprous chloride may be prepared as follows: 800 cc. of the hydrochloric acid solution prepared by the Winkler method given above or 1200 cc. of the Sandmeyer solution is poured into about 4 liters of water, and the resulting precipitate is transferred to a graduated stoppered cylinder of 250 cc. capacity. After about two hours the precipitate and liquid which is above the 50 cc. mark is drawn off by means of a siphon and 7.5 per cent ammonium hydroxide is added up to the 250 cc. mark. The stopper is inserted, the cylinder is well shaken, and it is then allowed to stand for several hours. A solution prepared in this manner has so slight a tension that the latter may in nearly every case be disregarded.

Frischer suggests[193] the preparation of an ammoniacal solution of a cuprous salt by adding ferrous sulphate to an ammoniacal solution of cupric sulphate, but he gives no specific directions.

Moser and Hanika[194] state that the most suitable concentration for an ammoniacal solution is 11 to 12 parts of CuCl, 13 to 14 parts of NH_3, and 76 to 74 parts of water, and they regard[195] this solution as unquestionably more efficient than the acid solution.

Wollers[196] uses a solution containing 213 grams of ammonium chloride, 171 grams of cuprous chloride, and 360 cc. of ammonium hydroxide per liter.

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[192] *J. Gasbel.*, **57**, 169 (1914).

[193] *Chem. Ztg.*, **32**, 1005 (1908).

[194] *Loc. cit.*

[195] See also Ott, *Gas u. Wasserfach*, **68**, 367 (1925).

[196] *Loc. cit.*

Both acid and ammoniacal solutions of cuprous chloride have no considerable tension, so that this may be disregarded in analyses in which only approximate results are determined. In very exact determinations, however, the gases that have been in contact with the reagent must be freed from hydrogen chloride or from ammonia.

The solutions of cuprous chloride may conveniently be used in the Hempel double pipettes for liquid reagents (Fig. 39).

If, after the absorption of carbon monoxide in a gas mixture, the hydrogen is to be determined with palladium, the ammoniacal solution must be used. If the amount of carbon monoxide alone is to be ascertained, the hydrochloric acid solution may be employed with equally good results.

Hainsworth and Titus[197] have found that carbon monoxide may be absorbed by a solution of cuprous ammonium carbonate that is prepared by agitating with air a solution containing about 15 per cent of ammonium carbonate and 5 per cent of ammonium hydroxide by weight, in a tower filled with copper turnings until the copper content of the solution is about 3.5 per cent. The solution may also be regenerated by heating to 75° in an inert atmosphere. Larsen and Teitsworth[198] investigated both the cuprous ammonium carbonate and cuprous ammonium formate solutions as absorbents for carbon monoxide. They found that at equivalent concentrations the two solutions have about the same absorption capacity, but the latter solution is much more stable.

Damiens[199] states that by moistening cuprous oxide with a little water and adding sulphuric acid in small portions, it is possible to prepare cuprous sulphate which is fairly stable in concentrated sulphuric acid. A 5 per cent solution by volume of this reagent in concentrated sulphuric acid is a good absorbent for carbon monoxide. It also absorbs oxygen, ethylene and acetylene, but not nitrogen, methane and its homologues, nor hydrogen. It is advisable to use two pipettes as is done with solutions of cuprous chloride. Lebeau and Bedel[200] find that this reagent is more efficient if a little β-napthol is added. They prepare the reagent by introducing 10 grams of β-napthol and a suspension of 5 grams of cuprous oxide in 95 grams of sulphuric acid (sp. gr. 1.84) and five grams of water into a 125 cc. flask and stirring the mixture mechanically for several hours. The solution is filtered through asbestos that has previously been washed with sulphuric acid and water, and dried. The solution is then allowed to stand for a few days and is decanted. One cc. will absorb 18 cc. of carbon monoxide, and when not more than two parts carbon monoxide to one part cuprous sulphate are absorbed, the compound is stable even at 100°. The same gases are absorbed by this reagent as by that of Damiens. De la Condamine[201] compared this reagent with both acid and ammoniacal cuprous chloride solutions as an absorbent for carbon monoxide, and found that Damiens' reagent is a more effective absorbent than either of the other two because the product that is formed is more stable; but the absorption takes place very slowly and requires about twice as many passages of the gas as with an acid solution of cuprous chloride. He further states that the acid solution of cuprous chloride is a better absorbent than the ammoniacal.

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[197] *J. Am. Chem. Soc.*, **43**, 1 (1921).
[198] *J. Am. Chem. Soc.*, **44**, 2878 (1922).
[199] *Compt. rend.*, **178**, 849 (1924).

Drehschmidt[202] has shown that the union of carbon monoxide with cuprous chloride is so feeble that upon shaking a solution that has taken up any considerable quantity of carbon monoxide, this gas is again given up in an atmosphere free from carbon monoxide. For this reason two pipettes are used in the absorption, one pipette containing a solution of cuprous chloride that has been in use some time, the other a solution that has been but little used.[203] In the absorption, the gas in question is first shaken for two minutes with the first-mentioned solution, is drawn back into the burette and is then passed into the second pipette containing the but slightly used solution, and is shaken three minutes therein. According to Drehschmidt, the ammoniacal solution is to be preferred to the hydrochloric acid one.

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[200] *Compt. rend.,* **179,** 108 (1924).
[201] *Compt. rend.,* **179,** 691 (1924).
[202] *Ber.,* **20,** 2344, 2752 (1887); **21,** 2158 (1888).
[203] Wollers, *Stahl u. Eisen,* **42,** 1050 (1922).

The results obtained by Gautier and Clausmann [204] in their experiments on the removal of carbon monoxide by absorption with cuprous chloride demonstrate the necessity of using two solutions of cuprous chloride as Drehschmidt recommends, and of *shaking* the gas with the absorbent, and furnish convincing evidence of the difficulty of effecting complete removal of carbon monoxide in the apparatus of Elliott or with the form of absorption pipette customarily employed in the Orsat apparatus. Producer gas contains a high percentage of carbon monoxide (sometimes as high as 30 per cent) and a comparatively small amount of hydrogen. In the analysis of such gas mixtures it should be borne in mind that the absorption of carbon monoxide by either of these reagents becomes quite slow even before these limits are reached. It is consequently of particular importance that record be kept of the volume of carbon monoxide that the absorbent has taken up, and that the absorbent be renewed before it has lost its efficiency.

Certain gases other than carbon monoxide are soluble to an appreciable degree in solutions of cuprous chloride. This renders it necessary, if accurate results are to be obtained, to saturate the cuprous chloride solution with those gases that are slightly soluble in it before proceeding to the absorption of carbon monoxide.

Solutions of cuprous chloride absorb not only carbon monoxide, oxygen and acetylene, but also the so-called heavy hydrocarbons. For this reason the heavy hydrocarbons, even if their determination is not desired, must be removed from the gas mixture before the carbon monoxide is absorbed by cuprous chloride. Failure to do this is a frequent cause of erroneous results. Manchot, König and Gall [205] state that

[204] *Compt. rend.,* **142**, 485 (1906).
[205] *Ber.,* **57**, 1157 (1924).

silver sulphate dissolved in concentrated sulphuric acid also takes up carbon monoxide readily and in large amounts. The maximum absorption was 0.86 mole of carbon monoxide per atom of silver in 33 per cent SO_3 acid at 0°.

Determination of Carbon Monoxide by Means of Iodine Pentoxide.—Nicloux [206] and Gautier [207] employ the reaction [208] between iodine pentoxide and carbon monoxide (see p. 238) for the quantitative determination of the latter substance. Kinnicut and Sanford [209] have shown that this method can be used for the determination of very small amounts of carbon monoxide not only in air, but also in illuminating gas. The gas mixture under examination must first be freed from unsaturated hydrocarbons, hydrogen sulphide, sulphur dioxide, and similar reducing gases. To accomplish this, Kinnicut and Sanford pass the gas through two U-tubes, one containing sulphuric acid [210] and the other small pieces of potassium hydroxide.[211] The purified gas is then passed through a small U-tube containing 25 grams of iodine pentoxide.

The iodine pentoxide may be prepared by the chloric acid method; [212] the tubes should be thoroughly dehydrated at 200° to 210° before use to prevent a high "blank" determination.[213]

Inasmuch as this substance acts upon cork, rubber, and the usual lubricants, Morgan and McWhorter later suggested [214] that the iodine pentoxide be placed in a U-tube with side arms, and that the large ends of the U-tube be then sealed before the blast lamp. The U-tube is suspended in an oil bath and its exit tube is joined to a Wolff absorption tube or similar apparatus (see p. 234) containing 0.5 gram of potassium iodide dissolved in 5 cc. of water. The oil bath is heated to 150° C. The temperature should not be allowed to rise much beyond 150° C., for Nowicki[215] has found that iodine pentoxide itself begins to decompose at 165° and is completely broken down at 300°. He also states that the oxidation of carbon monoxide by iodine pentoxide begins at 45° and is complete at 88°. From 250 cc. to 1000 cc. of the gas mixture under examination is then passed through the apparatus at the rate of about one liter in two hours. The iodine that is set free in the reaction is absorbed by the solution of potassium iodide.

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[206] *Compt. rend.*, **126**, 746 (1898).

[207] *Ibid.*, **126**, 931 (1898); *Bull. soc. chim.*, **17**, 256 (1915).

[208] Ditte, *Bull. soc. chim.*, **13**, 318 (1870).

[209] *J. Am. Chem. Soc.*, **22**, 14 (1900).

[210] It would be preferable to place the sulphuric acid in a Friedrichs spiral gas washing-bottle (see p. 119).

[211] See also Weiskopf, *J. Chem. Met. Soc. S. Africa*, **9**, 258, 306 (1909); Gontal, *Ann. chim. anal.*, **15**, 1 (1910); Levy, *J. Soc. Chem. Ind.*, **30**, 1437 (1911).

[212] Lamb, Bray and Geldard, *J. Am. Chem. Soc.*, **42**, 1636 (1920).

[213] Davies and Hartley, *J. Soc. Chem. Ind.*, **45**, 164 (1926).

[214] *J. Am. Chem. Soc.*, **29**, 1589 (1907).

Kinnicut and Sanford determined the amount of carbon monoxide in the gas mixture by titrating the free iodine with 0.001 *N* solution of sodium thiosulphate; 0.002266 gram of iodine is equivalent to one cc. of carbon monoxide measured under standard conditions.

In the reaction between iodine pentoxide and carbon monoxide, one cc. of carbon monoxide yields one cc. of carbon dioxide which in the above method passes through the solution of potassium iodide. Morgan and McWhorter[216] recommend that as a check upon or substitute for the iodine titration, the liberated carbon dioxide be determined. This they do by passing the gas that issues from the Wolff tube through an absorption apparatus[217] containing 50 cc. of a solution of barium hydroxide such as is used in the Hesse method for the determination of carbon dioxide in air, and determining the volume of the absorbed carbon dioxide by titration with a standard solution of oxalic acid that contains 1.1265 grams of crystallized oxalic acid per liter. Five cc. of this solution is equivalent to one cc. of carbon dioxide measured under standard conditions. Phenolphthalein, one part in 250 parts of alcohol, is used as indicator.

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[215] *Oesterr. Z. Berg-Hüttenw.*, **54**, 6 (1906).

[216] *Loc. cit.*

[217] They used a long test tube (24 x 2.5 cm.). This might advantageously be replaced by a glass cylinder about 20 cm. high and 4 cm. internal diameter, fitted with a three-hole rubber stopper, carrying an inlet and exit tube, and the tip of a burette. Such an arrangement would permit of the titration of the solution of barium hydroxide without transferring it to another container and thus exposing it to the air.

Graham and Winmill[218] have described a modification of Haldane's apparatus (see p. 417) in which carbon monoxide is oxidized to carbon dioxide, and that gas is determined by absorbing it in a solution of caustic potash and measuring the contraction. They state that the tube containing iodine pentoxide should not be heated above 100°, and that if over 12 per cent of hydrogen is present the sample must be diluted with air. In a later article Graham[219] proposes some further modifications in the procedure and apparatus. Sinnatt and Cramer[220] also determine carbon monoxide by oxidizing it with iodine pentoxide, absorbing the resulting carbon dioxide in barium hydroxide, and titrating the excess with hydrochloric acid.

Seidell[221] describes a special form of apparatus for this analysis. He determines the carbon monoxide by titrating the liberated iodine, and states that the carbon dioxide check is of no special value. On the other hand, Froboese[222] determines the carbon dioxide by absorbing it in barium hydroxide and titrating the excess, or converting the barium carbonate into barium sulphate. He also finds that the tube containing iodine pentoxide should be heated to 100°. The iodine titration method gives satisfactory results in the examination of atmospheric air of low carbon-monoxide content only when air free from carbon monoxide and carbon dioxide is passed through the apparatus for one hour at 100°

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[218] *J. Chem. Soc.*, **105**, 1996 (1914).
[219] *J. Soc. Chem. Ind.*, **38**, 10 (1919).
[220] *Analyst*, **39**, 163 (1914).
[221] *Ind. Eng. Chem.*, **6**, 321 (1914).
[222] *Z. anal. Chem.*, **54**, 1 (1915).

before introducing the gas and for the same length of time after the reaction.

Davies and Hartley[223] titrate the liberated iodine and state that any temperature between 120° and 150° is satisfactory if the tube of iodine pentoxide is properly manipulated.

The above method for the determination of carbon monoxide by the use of iodine pentoxide gives very accurate results if the carbon monoxide is present in quite small amounts. By means of it one part of carbon monoxide in 40,000 parts of air may be determined in as small an initial volume of air as one liter. It is, however, not suited to the determination of large amounts of carbon monoxide, as Gill and Bartlett have shown[224] in their examination of the method of Smits, Raken and Torwogt[225] who had proposed the employment of the method for the determination of carbon monoxide in illuminating gas.

Colorimetric Determination of Carbon Monoxide.—Haldane has devised[226] a colorimetric method for the determination of small amounts of carbon monoxide in air. The method is based upon the fact that when oxygen and carbon monoxide are passed through a blood solution the amounts of oxyhæmoglobin and carbon monoxide hæmoglobin that are formed are in the ratio of the partial pressures of these two gases in the air, multiplied by a constant. The percentage of oxygen in the gas mixture can easily be determined by analysis, and if the value of the constant is known, the percentage of carbon monoxide in the gas can then be calculated from the relative amounts of oxyhæmoglobin and carbon monoxide hæmoglobin that are formed in a solution of blood through which the gas mixture in question has been passed.

A dilute solution of oxyhæmoglobin is of a yellow color, while that of carbon monoxide hæmoglobin is pink. The two solutions required for the colorimetric determination are: (1)

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[223] *Loc. cit.*
[224] *Ind. Eng. Chem.*, **2**, 9 (1910).
[225] *Z. angew. Chem.*, **13**, 1002 (1900).
[226] *J. Physiol.*, **18**, 461 (1895).

A five per cent solution of defibrinated blood. This solution should be freshly prepared and should be kept in a stoppered bottle. (2) A solution of carmine, which is prepared by grinding one gram of carmine with a few drops of ammonium hydroxide in a mortar and dissolving the substance in 100 cc. of glycerine. Ten cc. of this liquid diluted to one liter with water forms the standard solution.

The air under examination is drawn through a bottle of about 200 cc. capacity fitted with a three-hole rubber stopper. In two of the openings of the stopper are inserted the inlet and outlet tubes for the passage of the air, and the third is closed by a glass plug. After the air originally in the bottle has been completely displaced by the air under examination, the rubber tubes attached to the glass tubes of the bottle are closed by pinchcocks. The glass rod closing the third opening in the stopper is then removed, and there is inserted through this opening the tip of a small pipette that contains about five cc. of the blood solution. This solution is allowed to run down into the bottle, the pipette is withdrawn, the opening in the stopper is again closed with a plug, and the flask is gently shaken for about five minutes.

The blood solution is then transferred to a small colorimeter tube. In a second colorimeter tube of exactly the same dimensions, five cc. of the original blood solution is placed, and in a third tube five cc. of the blood solution that has been saturated with carbon monoxide by shaking the blood with coal gas. The standard carmine solution is now run from a burette into the second colorimeter tube until the color of the liquid is identical with that of the solution that has been saturated with carbon monoxide. The carmine solution is then added to the contents of the first test tube until the same tint is produced.

If x cc. of the carmine solution were run into a second tube, and y cc. into the first tube, then

$$\frac{y}{y+5} \times \frac{x+5}{x} \times 100 = S,$$

in which S is the percentage saturation of the blood that has been shaken with the air under examination. The amount of carbon monoxide in the air may then be calculated from the following table:

TABLE XIII

Percentage Saturation	Carbon Monoxide in Air
10	0.015 per cent
20	0.04 "
30	0.08 "
40	0.12 "
50	0.16 "
60	0.22 "
70	0.30 "
80	0.60 "
90	1.2 "

The method is stated to give fairly accurate results for amounts of carbon monoxide in air between 0.015 and one per cent. With more than one per cent of carbon monoxide the gas should be diluted with air that is free from carbon monoxide.

Sayers and Yant [227] have described a colorimetric method which is based upon the fact that when normal blood, diluted 1:4 with water and shaken with an equal volume of a one per cent solution of tannic acid, is allowed to stand for twenty-four hours, a grey suspension is formed, whereas blood containing carbon monoxide hæmoglobin remains carmine red. Standards may be prepared from blood, but as these are reliable only for a limited time, it is preferable to prepare permanent standards from pigments corresponding to the blood colors. These vary from 0 to 100 per cent carbon monoxide hæmoglobin in steps of 10.

The sample of air is collected in a 250 cc. bottle into which it is driven by means of a rubber aspirator bulb to which a soda-lime scrubber is attached. A rubber stopper is then inserted in the bottle. 2 cc. of a dilute solution (1:20) of fresh human or animal blood is introduced into the bottle, and the bottle is rotated constantly in a horizontal position for fifteen to twenty minutes. When equilibrium is reached, the solution is poured into a test tube, and approximately 0.04 gram of a mixture of equal parts by weight of tannic acid and pyrogallol is added in the solid form or in solution. The tube is inverted several times to insure thorough mixing and is then placed in a rack and allowed to stand for 15 minutes at room temperature. It is then compared with the standards until the one is found which most nearly matches it.

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[227] *Bureau of Mines, Tech. Paper* 373 (1925).

When equilibrium has been established between carbon monoxide and oxygen and hæmoglobin, the amount of hæmoglobin combined with each depends on the product of the affinity, a, times the partial pressure, p, and the ratio of the amounts can be expressed by the following equation:

$$\frac{\text{Amount combining with CO}}{\text{Amount combining with } O_2} \quad \text{or} \quad \frac{\text{HbCO}}{\text{HbO}_2} = \frac{\text{p CO} \times \text{a CO}}{\text{p } O_2 \times \text{a } O_2}$$

where

HbCO is the value determined by the analysis of the blood,

$\text{HbO}_2 = 100 - \text{HbCO}$,

p O_2 = in normal air 20.93 per cent by volume or 2,093 parts per 10,000. If, however, the oxygen content is determined, the actual value is used.

a $O_2 = 1$,

a CO = 300 on the basis of a $O_2 = 1$.

Solving for p CO,

$$\text{p CO} = \frac{\text{HbCO}}{100 - \text{HbCO}} \times \frac{2093}{300}.$$

Thus if a blood solution was found to contain 50 per cent of carbon monoxide hæmoglobin by comparison with the standards, then the carbon-monoxide content is

$$\frac{50}{100 - 50} \times \frac{2093}{300} = 0.07 \text{ per cent.}$$

For other colorimetric methods see under the methods of detecting carbon monoxide.

Determination of Carbon Monoxide by Fractional Combustion.—Nesmjelow[228] has made an exhaustive study of the fractional combustion of carbon monoxide in the presence of hydrogen and methane. He summarizes the results of his experiments as follows:

(1) That when hydrogen mixed with air is passed through a U-shaped tube that contains palladium asbestos and stands at the temperature of the room, the hydrogen is burned completely upon a single passage of the gas mixture through the tube;

(2) That when a mixture of hydrogen, carbon monoxide and air is passed through the U-tube, both the hydrogen and carbon monoxide (in the proportions in which he used them) burn completely without previous warming of the palladium asbestos. It is thus easily possible to determine hydrogen and carbon monoxide by combustion over palladium asbestos, and ascertaining the contraction and the volume of carbon dioxide formed;

(3) That the combustion of carbon monoxide under the above conditions begins at 120°, while that of methane does not begin below 150°, and that if a mixture of hydrogen, carbon monoxide, methane and air is passed through the palladium asbestos tube, at a speed not exceeding one liter per hour, hydrogen and carbon monoxide will be completely oxidized and methane will not be attacked. If the speed of flow of the gas mixture be increased, the rise of temperature in the U-tube, resulting from the more active combustion, may cause some of the methane to burn and thus render the results worthless.

Nesmjelow then described a method, original with him, for the fractional combustion of carbon monoxide by means of copper oxide. Copper oxide, mixed with asbestos fibers, is heated to dark redness and, after cooling in a desiccator, is placed in a small U-tube of hard glass. This is connected at the two ends with a gas burette and pipette in the usual manner, and a sand bath is then brought up under it and the lower part of the tube is covered with the sand. The bath is heated to 250°, and the mixture of hydrogen, carbon monoxide, methane and air passed through it about six times. The sand bath is then removed and the gas cooled to the temperature that it had at the beginning. The volume is measured and then the carbon dioxide that has been formed is determined by absorption. From these data the carbon monoxide and the hydrogen (which of course burns also) are calculated. At the above temperature methane is not oxidized. The speed of flow of the gases through the U-tube has no effect upon the accuracy of the separation.

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[228] *Z. anal. Chem.*, **48**, 232 (1909).

For a complete discussion of the methods of determining carbon monoxide by fractional combustion the reader is referred to Chapter XIII.

A method for the fractional combustion of carbon monoxide [229] consists in passing the gas mixture over yellow mercuric oxide contained in a U-tube of dark glass and maintained at 100° by immersing it in boiling water. The carbon dioxide is absorbed in a standard solution of barium hydroxide. Methane is unaffected at 100°. Hydrogen is partially oxidized but this does not influence the titration.

METHANE (CH_4)

Marsh-gas, Fire-damp

Properties of Methane. — Specific gravity (air = 1), 0.5545; density at 0°, 760 mm., 0.7168 grams per liter; critical temperature, — 82.85°; critical pressure, 45.6 atmospheres; boiling point, — 161.4°; melting point, — 184°. According to Winkler [230] one volume of water absorbs at 760 mm. and at

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[229] Moser and Schmid, *Z. anal. Chem.*, **53**, 217 (1914).
[230] *Ber.*, **34**, 1408 (1901).

0°, 0.05563 vol. methane
5°, 0.04805 " "
10°, 0.04177 " "
15°, 0.03690 " "
20°, 0.03308 " "
25°, 0.03006 " "
30°, 0.02762 " "

Detection of Methane.—Due to the possibility of explosions in coal mines caused by the ignition of mixtures of methane and air, the detection of the presence of this gas is of very great importance. Probably the most used method is the modified Davy lamp,[231] but more accurate methods are desirable. According to Hofmann,[232] if the lamp is filled with alcohol containing one per cent of dichlorethylene, 0.2 per cent of copper chloride and 0.2 per cent of magnesium chloride, the cap of the flame is colored an intense blue when more than one per cent of methane is present. The United States Bureau of Mines has developed a detector[233] in which the methane is burned with air by means of a hot platinum spiral.

Hauser and Herzfeld[234] have described a method for the detection of methane which is based on the fact that methane and ozone react to form formaldehyde. The presence of formaldehyde may be detected by its odor. The formaldehyde may be absorbed by moist glass wool and determined by the morphine-sulphuric acid reaction.

Determination of Methane.—Methane may be determined by explosion with oxygen or air (see p. 138), by combustion with copper oxide (see p. 157), by combustion in the Dreh-schmidt platinum capillary tube (see p. 149) or by combustion in the Dennis pipette (see p. 143).

$$(1)\qquad \begin{array}{ccccccc} CH_4 & + & 2\ O_2 & = & CO_2 & + & 2\ H_2O \\ \text{1 vol.} & & \text{2 vol.} & & \text{1 vol.} & & \text{liquid} \end{array}$$

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[231] *U. S. Bureau of Mines, Bulletin* 227 (1924).

[232] Hofmann, *Lehrbuch der anorganischen Chemie* (1928), p. 321.

[233] Burrell, *Ind. Eng. Chem.*, **8**, 365 (1916); Milligan, *U. S. Bureau of Mines, Tech. Paper* 357 (1925).

[234] *Ber.*, **45**, 3515 (1912); **48**, 895 (1915).

The amount of methane may be ascertained either by determining the volume of carbon dioxide that is formed, which will equal the volume of the methane, or by absorbing the carbon dioxide without measuring it and ascertaining the total diminution in volume, one-third of which will equal the volume of the methane.

In the opinion of the authors the method of determining methane with the combustion pipette is superior (a) to the explosion method because it permits of the combustion of the total residue and avoids the possibility of error through formation of oxides of nitrogen; (b) to the combustion with copper oxide because the latter calls for high and prolonged heating of the combustion tube; (c) and to the combustion with the Drehschmidt capillary because this method necessitates the use of a comparatively large volume of an explosive gas mixture, and further because of the tendency of the Drehschmidt tube to show leakage after a short period of use.

The combustion pipette and its level-bulb may be filled with water if no gases other than methane and nitrogen are present in the gas mixture; the methane is here determined by passing the gases, after combustion, into a potassium hydroxide pipette to completely remove the carbon dioxide and then calculating the methane from the total diminution in volume (see above).

If the combustion pipette and its level-bulb are filled with mercury and the gases are measured over mercury, then hydrogen, methane and nitrogen may be determined simultaneously by a single combustion by measuring the contraction after combustion and the volume of carbon dioxide that is formed.

A measured volume of the gas mixture is transferred to the combustion pipette and is burned in the usual manner by the slow addition of a measured amount of oxygen (see p. 145). The residual gas is then passed back into the burette and the contraction in volume is measured. The gas mixture is next passed into the potassium hydroxide pipette to absorb the carbon dioxide and is then again drawn back into the burette and measured.

Since one volume of methane produces, on combustion, one volume of carbon dioxide (see Equation 1), the volume of the methane in the gas mixture is equal to the volume of carbon dioxide formed.

Since

(2) $$\underset{\text{2 vols.}}{2\ H_2} + \underset{\text{1 vol.}}{O_2} = \underset{\text{liquid}}{2\ H_2O},$$

the contraction due to the combustion of hydrogen is equal to $\frac{3}{2}$ the volume of hydrogen in the gas mixture. The contraction due to the combustion of methane (see Equation 1) is equal to twice the volume of the carbon dioxide formed. Consequently the total contraction in the gas volume that results when a mixture of hydrogen and methane is burned may be represented by the expression

$$\text{Contraction} = \tfrac{3}{2}\ H_2 + 2\ CO_2$$

or $$\tfrac{3}{2}\ H_2 = \text{Contraction} - 2\ CO_2$$

or $$\text{vol. } H_2 = \tfrac{2}{3}\ (\text{Contraction} - 2\ CO_2)$$

The volume of hydrogen in the gas mixture is therefore found by subtracting twice the volume of carbon dioxide formed in the combustion from the total contraction, and taking two-thirds of the remainder.

Hydrogen, methane, carbon monoxide and nitrogen may be determined by a single combustion if, in addition to the measurement of the total contraction and of the volume of carbon dioxide formed, the volume of oxygen consumed in the combustion is ascertained.

The combustion is carried on exactly in the manner described above for a mixture of hydrogen, methane and nitrogen except that after the carbon dioxide has been absorbed and the residue measured, the excess of oxygen is determined by passing the gas residue into a pipette containing alkaline pyrogallol or sodium hyposulphite and subtracting this result from the total volume of oxygen added. The difference is the oxygen consumed in the combustion. Having thus ascertained the contraction resulting from the combustion, the volume of carbon dioxide formed, and the amount of oxygen consumed, we have all the data necessary for the calculation of the amounts of carbon monoxide, hydrogen, methane and nitrogen existing in the original mixture.

The volume changes that result from the combustion of hydrogen and methane are shown in Equations 1 and 2 (see above). When carbon monoxide is burned, two volumes of the gas unite with one volume of oxygen to form two volumes of carbon dioxide.

$$(3) \qquad \underset{\text{2 vols.}}{2\ CO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{2 vols.}}{2\ CO_2}.$$

From these three equations the following expressions may be derived:

$$\text{Contraction} = \tfrac{1}{2}\ CO + \tfrac{3}{2}\ H_2 + 2\ CH_4.$$
$$\text{Carbon dioxide formed} = CO + CH_4.$$
$$\text{Oxygen consumed} = \tfrac{1}{2}\ CO + \tfrac{1}{2}\ H_2 + 2\ CH_4.$$

From these last three equations a variety of formulas for the calculation of the various components of the original mixture may be derived. Noyes and Shepard give:

(1) H_2 = Contraction minus oxygen consumed.
(2) CO = $\tfrac{2}{3}$ ($2\ CO_2 + 1\tfrac{1}{2}\ H_2$ minus oxygen consumed).
(3) $CH_4 = CO_2 - CO$.
(4) N_2 = Original volume $- (H_2 + CO + CH_4)$.

Instead of (2) and (3) we may also use:

$$CO = CO_2 - CH_4.$$
$$CH_4 = \frac{2\ \text{Contraction} - CO_2 - 3\ H_2}{3}.$$

If no nitrogen is present in the original mixture the following equations of Vignon may be employed, V representing the volume of the gas mixture taken for the combustion.

$$\begin{aligned} H_2 &= V - CO_2. \\ CO &= \tfrac{1}{3}\ CO_2 + V - \tfrac{2}{3}\ \text{contraction}. \\ CH_4 &= \tfrac{2}{3}\ CO_2 + \tfrac{2}{3}\ \text{contraction} - V. \end{aligned}$$

Hempel states[235] that he has found it difficult to obtain complete combustion of methane with the Dennis combustion pipette when methane is mixed with nitrogen. He asseverates that when the ordinary procedure is followed, a part of the methane may escape combustion, and that for complete combustion it is necessary to maintain the spiral at red heat for a considerable length of time, which causes surface oxidation of the mercury in the pipette, and, as a consequence, too high contraction. There is no doubt that this error would result if the spiral were subjected to prolonged heating, but experience of several years with the combustion pipette leads the authors to believe that the maintenance of the spiral at red heat for sixty seconds after the introduction of the gas suffices in all cases for complete combustion of the methane. When the spiral is heated for so brief a time no appreciable oxidation of the mercury in the pipette results.

Murmann[236] determines very small quantities of methane by burning the gas mixture, freed from carbon dioxide, by means of hot copper oxide, and determining the resulting carbon dioxide by absorption in a standard solution of barium hydroxide containing 0.5 to 1 cc. of a one per cent solution of gelatin, and then titrating the solution.

THE HEAVY HYDROCARBONS

As used in technical gas analysis, the term "heavy hydrocarbons" comprises gases of the series, C_nH_{2n} (the olefines), such as ethylene, C_2H_4, propylene, C_3H_6, and butylene, C_4H_8; of the series C_nH_{2n-2}, such as acetylene, C_2H_2; and of the series C_nH_{2n-6} such as benzol (benzene), C_6H_6 and toluol (toluene) C_7H_8.

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[235] *Z. angew. Chem.*, **36**, 1841 (1912).

[236] *Oesterr. Chem. Ztg.*, **17**, 69 (1914); **25**, 90 (1922).

The heavy hydrocarbons are the chief illuminants in coal gas or carburetted gas, and for this reason their determination is of importance when the gas is to be used directly for illuminating purposes.

Absorption of Heavy Hydrocarbons.—All of these gases are absorbed by fuming sulphuric acid of about 1.94 specific gravity containing about 24 per cent free sulphur trioxide at 15°. The acid is placed in a special absorption pipette of the form shown in Fig. 37.

To effect the removal of the heavy hydrocarbons, the glass caps on the pipette are removed, and a short piece of small rubber tubing, such as is used on the other gas pipettes, is slipped upon *C*. A pinchcock is placed upon this rubber tube. The acid in the pipette is driven up in the capillary to the point marked *H* by blowing through a rubber tube that has been attached to the end *A*, and the pinchcock is closed. The pipette and gas burette are then connected by an empty, dry capillary tube of the usual form. The gas mixture is then slowly passed over into the pipette, and after a few seconds is slowly drawn back into the burette. This is repeated three times or more, the number of passages of the gas depending upon the per cent of the heavy hydrocarbons present and the strength of the acid. Throughout the operation the fuming sulphuric acid should never be drawn above the point *H* in the capillary of the pipette. When the gas is drawn back into the burette the last time, the acid in the pipette should be brought exactly to the point *H*. The pinchcock at the top of the burette is now closed. The diminution in the gas volume may not yet be read off on the burette because of the presence in the gas of sulphur trioxide from the fuming acid in the pipette. This, together with any sulphur dioxide that may have been formed during the absorption, is removed by passing the gases into a pipette filled with potassium hydroxide (see p. 231). The gas is then drawn back into the burette and the decrease in volume noted.

The moisture content of the gas, after it has been brought into contact with the fuming sulphuric acid and the potassium hydroxide, will of course be less than at the beginning of the determination when the gas was "saturated" with water vapor. To avoid error from this cause in the final measurement, the gas must in this, as in all other similar absorptions, finally be read over water or over mercury upon which stands a drop of water.

This method of manipulation introduces slight errors in the results for those gases that are determined after the heavy hydrocarbons are removed, because the connecting capillary tube and the upper part of the capillary of the pipette are filled with air when the burette and pipette are connected. The volume of air in the capillaries is, however, so small [237] that the errors arising from this source may be disregarded in technical analyses.

Worstall [238] states that, on prolonged contact, fuming sulphuric acid absorbs a little methane and ethane, but the error is negligible unless the time of absorption is over fifteen minutes. Anderson and Engelder [239] have observed that this reagent has a marked tendency to absorb gasoline vapor. Ott [240] states, however, that fuming sulphuric acid is preferable to bromine water as an absorbent, being more convenient and giving lower errors due to incomplete absorption.

These gases may also be absorbed by a solution of bromine in water. After treatment with this reagent, the gas must be passed into a pipette containing a solution of caustic potash to remove the bromine vapor before the decrease in volume is measured (see p. 231).

Piechota [241] has recommended the use of a cold, saturated solution of potassium dichromate in concentrated sulphuric acid as an absorbent for these gases. This reagent does not attack mercury which may therefore be used for confining the gas.

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[237] The length of the empty capillary tube need not exceed 16 cm. which has a volume of only 0.16 cc.

[238] *J. Am. Chem. Soc.*, **21**, 245 (1899).

[239] *Ind. Eng. Chem.*, **6**, 989 (1914).

[240] *Gas u. Wasserfach*, **68**, 367 (1925).

[241] *Chem. Ztg.*, **44**, 797 (1920).

ETHYLENE (C_2H_4)

Properties of Ethylene. — Specific gravity (air = 1), 0.9684; density at 760 mm., 0°, 1.2609 grams per liter; critical temperature, 9.5°; critical pressure, 50.65 atmospheres; boiling point, — 103.9°; melting point, — 169.4°. One volume of water absorbs at 760 mm. and at

0°, 0.226 vol.
5°, 0.191 "
10°, 0.162 "
15°, 0.139 "
20°, 0.122 "
25°, 0.108 "
30°, 0.098 "

Determination of Ethylene by Absorption. — Bromine water absorbs the gas rapidly and completely;[242] the vapor of bromine must be removed after the absorption by passing the gas into a potassium hydroxide pipette. The reagent is prepared by diluting saturated bromine water with twice its volume of water. It then contains about one per cent of bromine. The liquid is placed in a Hempel double absorption pipette for liquid reagents (Fig. 39) with water in the last two bulbs.

Suida and Wesely[243] state that only by using a 0.04 per cent bromine water and diluting the gas with air, were they able to get constant results. The gas mixture was shaken with the reagent for six to eight minutes. By this treatment the absorbed gases are chiefly, if not wholly, olefines of the ethylene series.

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[242] Treadwell and Stokes, *Ber.*, **21**, 3131 (1888); Haber and Oechelhäuser, *ibid.*, **29**, 2700 (1896).

[243] *Z. anal. Chem.*, **64**, 143 (1924).

The usual absorbent for ethylene is fuming sulphuric acid, ethionic acid, $C_2H_5S_2O_7$, being formed. Lebeau and Damiens[244] and Wellers[245] use a solution of one gram of vanadic acid or 6 grams of uranyl sulphate in 100 grams of concentrated sulphuric acid (sp. gr. 1.84) for the absorption of the gases of the ethylene series. The determination is carried out in the manner described on page 260.

Determination of Ethylene in Presence of Acetylene.—Tucker and Moody state[246] that ethylene may be determined in mixture with acetylene by passing the gases through an ammoniacal silver solution which removes acetylene completely but absorbs only a relatively small amount of ethylene. The method is not exact but it might prove useful in an approximation of the percentages of ethylene and acetylene in a mixture of the two gases. The ammoniacal silver solution that is used in this separation is prepared by dissolving 10 grams of silver nitrate in 500 cc. of distilled water, adding dilute hydrochloric acid until the solution is barely acid to litmus paper, and then adding ammonium hydroxide until the solution is slightly ammoniacal. When acetylene is absorbed by this solution, silver acetylide, Ag_2C_2, is formed.

Separation of Ethylene from Benzene.—The separation of ethylene from benzene may according to Haber and Oechelhäuser,[247] be accomplished by means of bromine water which removes the ethylene completely but does not appreciably attack the benzene if the contact between gas and reagent is not prolonged beyond two minutes. Some benzene vapor is, however, mechanically carried down by the bromine vapor, and for this reason the method does not yield very accurate results.

Taplay[248] finds that the olefines may be separated from benzene if an aqueous solution of bromine is used, but a solution of potassium bromide absorbs benzene also.

[244] *Compt. rend.*, **156**, 557 (1913).

[245] *Stahl u. Eisen*, **42**, 1449 (1922).

[246] *J. Am. Chem. Soc.*, **23**, 671 (1901).

[247] *J. Gasbel.*, **39**, 799 (1896); **43**, 347 (1900).

[248] *J. Gas Lighting*, **124**, 870 (1913).

Separation of Ethylene from Butylene.—Fritzsche states[249] that ethylene may volumetrically be separated from butylene by means of sulphuric acid of 1.62 specific gravity which absorbs butylene but not ethylene.

According to Suida and Wesely,[250] ethylene may be separated from its homologues by treatment with 87 per cent sulphuric acid, providing the gas mixture does not contain more than 25 per cent of olefines. Wellers,[251] on the other hand, says that it is impossible to separate the gases of the ethylene series by treatment with sulphuric acid of various concentrations at room temperature. However, the unsaturated hydrocarbons may easily be converted into saturated compounds by passing them at room temperature over palladium that is saturated with hydrogen, and then separating the products by fractional distillation at low temperatures.

PROPYLENE (C_3H_6)

Specific gravity, 1.4527; weight of one liter, 1.878 grams. The gas may be determined by absorption with fuming sulphuric acid or by combustion. Details of these methods are given on pages 260 and 143.

ACETYLENE (C_2H_2)

Properties of Acetylene.—Specific gravity (air = 1), 0.8988; density at 0°, 760 mm., 1.1791 grams per liter; critical temperature, 35.5°; critical pressure, 61.65 atmospheres; boiling point, —83.6° melting point, —81.8°.

Acetylene is quite soluble in a number of liquids.[252] At 18° and 760 mm., 1 vol. of water and carbon disulphide dissolve 1 vol. of acetylene, oil of turpentine and carbon tetrachloride 2; amyl alcohol and styrol 3.5; chloroform and benzene 4; absolute alcohol and acetic acid 6; and acetone 25.

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[249] *Z. angew. Chem.*, **456** (1896).

[250] *Loc. cit.*

[251] *Loc. cit.*

[252] Vogel, *Handbuch für Acetylen*, p. 152.

At 15° and 12 atmospheres acetone dissolves 300 volumes and at — 80° and 760 mm., 2000 volumes.

It is slowly absorbed by concentrated sulphuric acid, acetyl sulphonic acid, $C_2H_4SO_4$, being formed. An ammoniacal solution of cuprous chloride absorbs the gas rapidly and there is formed a brown to violet-red precipitate of copper acetylide, Cu_2C_2, which explodes when heated or struck. Acetylene produces in an ammoniacal silver solution [253] a white precipitate, Ag_2C_2, which is even more explosive than the copper acetylide. If the gas is led into ammoniacal solutions of aurous thiosulphate or potassium mercuric iodide, exceptionally explosive compounds are formed.

All of the ammoniacal solutions of metals that have been mentioned may be used as absorbents for acetylene.

Determination of Acetylene.—Although acetylene may be determined by combustion with oxygen, this method cannot usually be employed because the gas occurs in mixtures with other combustible gases. One volume of acetylene yields on combustion 2 volumes of carbon dioxide. When 2 volumes of acetylene are burned there is a contraction of 3 volumes.

$$\begin{array}{cccc} 2\ C_2H_2 + & 5\ O_2 = & 4\ CO_2 + & 2\ H_2O. \\ \text{2 vols.} & \text{5 vols.} & \text{4 vols.} & \text{liquid.} \end{array}$$

It is best determined by leading it through an ammoniacal cuprous chloride solution, a reddish brown precipitate being thrown down.[254] The precipitate is filtered off, and is washed with water containing ammonia until the wash-water passes through colorless. The moist copper acetylide may be collected in a Gooch crucible and dried over calcium chloride at 100° in a current of carbon dioxide [255] and weighed as Cu_2C_2. Dry copper acetylide may, however, explode at a temperature as low as 60°.

The acetylene may be determined, without danger of explosion, by taking advantage of the fact that the moist precipitate contains carbon and copper[256] in the atomic proportion of 1:1, and determining the copper in the moist compound. This is done by pouring hydrochloric acid upon the precipitate which is thereby decomposed with evolution of acetylene. As it is difficult to completely decompose the copper acetylide, the end of the reaction is not waited for, but the rest of the precipitate, without being washed, is dried on the filter and ignited. The copper oxide is dissolved in a few drops of nitric acid, and this solution is added to the hydrochloric acid filtrate first obtained. The copper in the solution may then be determined electrolytically, or it may be precipitated from hot solution with sodium hydroxide, filtered off, washed, ignited and weighed as cupric oxide.[257]

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[253] The method of preparing this solution is described under Ethylene, p. 263.

[254] Ilosvay, *Ber.*, **32**, 2698 (1899).

[255] Scheiber, *Z. anal. Chem.*, **48**, 537 (1909).

Willstätter and Maschmann[258] have so modified this method as to permit of the determination of acetylene volumetrically. The copper acetylide is filtered off on asbestos and is washed to remove the excess of ammonium hydroxide, until the wash-water remains pink on the addition of one drop of 0.1 *N* potassium permanganate. Oxidation by air must be avoided during the washing. The moist precipitate is dissolved from the filter with about 25 cc. of an acidified solution of ferric sulphate.

$$Cu_2C_2 + Fe_2(SO_4)_3 + H_2SO_4 = 2\,FeSO_4 + 2\,CuSO_4 + C_2H_2,$$

and the filtrate is titrated with a 0.1 *N* solution of potassium permanganate.

Weaver[259] has described a colorimetric modification of this method. The gas mixture is passed through a solution prepared as follows: 0.25 gram of gelatin is dissolved in hot water and diluted to 500 cc.; this is mixed with 500 cc. of 95 per cent alcohol, and 1.25 grams of hydroxylamine hydrochloride is added; 10 cc. of concentrated ammonium hydroxide and 0.01 to 0.02 gram of cuprous chloride are added to 20 cc. of the above solution.

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[256] Scheiber, *Ber.*, **41**, 3816 (1908).

[257] Muller, *Bul. soc. chim.*, **27**, 69 (1920); Arnold, Möllney and Zimmermann, *Bull. Ber.*, **53**, 1034 (1920).

[258] *Ber.*, **53**, 939 (1920).

[259] *J. Amer. Chem. Soc.*, **38**, 352 (1916); Schulze, *Z. angew. Chem.*, **29**, 341 (1916).

The resulting red colloid is compared colorimetrically with a standard composed of 0.21 mg. of chromanilbraun R, 0.04 mg. of carmoisine B, 2.5 grams of gum arabic, and 100 cc. of water. The method is so sensitive that amounts as small as 0.03 mg. may be detected. Hydrogen sulphide and large amounts of oxygen and carbon dioxide interfere with the test, but all of them may be removed by first passing the gas mixture through a hot solution of alkaline pyrogallol.

Ross and Trumbull[260] described a modified form of the Chavastelon method[261] for the determination of acetylene in the presence of ethylene, but Willstätter and Marchmann[262] later stated that methods based on this reaction lead to erroneous results. The procedure is based on the reaction,

$$C_2H_2 + 3\ AgNO_3 = Cu_2Ag_2 \cdot AgNO_3 + 2\ HNO_3.$$

An excess of standard alkali is added, then enough neutral sodium chloride to precipitate the dissolved silver, and the excess of alkli is titrated with standard hydrochloric acid, using methyl orange as indicator.

As an absorbent for acetylene and its homologues in the presence of gases of the ethylene and methane series, Lebeau and Damiens,[263] and Wellers[264] use a solution containing 25 grams of mercuric iodide and 30 grams of potassium iodide in 100 cc. of water, with the addition of a small fragment of potassium hydroxide. One cc. of this reagent absorbs 20 cc. of acetylene, forming a white precipitate.

Paal[265] has observed that acetylene is adsorbed by colloidal palladium and platinum, and also by palladium and platinum black.

[260] *J. Am. Chem. Soc.*, **41**, 1180 (1919).

[261] *Compt. rend.*, **125**, 245 (1897).

[262] *Loc. cit.*

[263] *Loc. cit.*

[264] *Loc. cit.*

[265] *Ber.*, **43**, 2684, 2692 (1910); **46**, 128 (1913); **48**, 1195 (1915).

Acetylene may be determined volumetrically in the Hempel apparatus by absorbing it with fuming sulphuric acid contained in the pipette shown in Fig. 37. It is necessary to pass the gas repeatedly into the pipette until no further diminution in volume is noted upon measuring the residual gas in the burette. Before making the final measurement, the gas must, of course, be passed into the potassium hydroxide pipette to remove the sulphur trioxide. Traces of acetylene may still remain in the gas mixture after this treatment with fuming sulphuric acid, and these may be removed by passing the gas into a pipette containing an ammoniacal solution of cuprous chloride. If oxygen is present with the acetylene, it is removed, after the treatment of the gas mixture with fuming sulphuric acid, by absorption with alkaline pyrogallol. Phosphorus cannot be used for the absorption of oxygen in the presence of even very small amounts of acetylene because the gas inhibits the union between oxygen and phosphorus to such an extent as to render it impossible to obtain even approximately correct results for oxygen with this reagent.

CYANOGEN (C_2N_2)

Properties of Cyanogen. — Specific gravity (air = 1), 1.7968; density at 0°, 760 mm., 2.3229 grams per liter; critical pressure, 59.75 atmospheres; critical temperature, 128.3°; boiling point, —20.5°; melting point, —34.4°.

One volume of water dissolves at 20°, 4.5 volumes of cyanogen; 1 volume of alcohol, 20 volumes of cyanogen.

Burned with twice its volume of oxygen it forms 2 volumes of carbon dioxide and 1 volume of nitrogen.

Detection of Cyanogen.—Free cyanogen, or dicyanogen, may be detected according to Kunz-Krause[266] by the Schönbein-Pagenstecher reaction. For carrying out this test, strips of filter paper are first dipped into a dilute aqueous solution of copper sulphate (1:1000), and are then impregnated with a 3 per cent tincture of gum guaiac. The paper thus prepared turns blue when acted upon by dicyanogen or hydrogen cyanide, but this blue color is also caused by certain oxidizing agents such as ozone and nitric acid.

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[266] *Z. angew. Chem.*, **26**, 652 (1901).

The reaction is somewhat sharper when the gas mixture, instead of being brought in contact with the paper above described, is passed through a wash bottle containing an alcoholic copper sulphate—gum guaiac solution.

The reaction has lately been increased in delicacy by Schaer, who uses guaiaconic acid in place of the gum guaiac. The reagent should always be freshly prepared, and this is done by adding to 10 cc. of a dilute aqueous copper sulphate solution 15 cc. of alcohol in which a little guaiaconic acid has previously been dissolved.

Brünnich states[267] that the delicacy of the Schönbein-Pagenstecher test for hydrogen cyanide may be greatly enhanced by moistening the paper with formalin instead of with water before exposing the paper to the gas mixture under examination. The color that here results if hydrogen cyanide is present is deep blue, whereas, if the paper is moistened with water, it is a light blue.

Another delicate reaction for dicyanogen is given by Kunz-Krause in the article above cited, this test depending upon the formation of isopurpuric acid or picrocyaminic acid, $C_8H_5N_5O_6$, from picric acid. 2 cc. of a cold saturated aqueous solution of picric acid (1:86) is mixed with 18 cc. of alcohol and 5 cc. of a 15 per cent aqueous solution of potassium hydroxide. When brought into contact with this solution pure cyanogen yields a deep purple-red color, which later turns to brown. On long standing the potassium salt of isopurpuric acid separates in the form of an oil of purple-red color. This reagent also must always be freshly prepared.

Potassium hydroxide absorbs cyanogen, potassium cyanide and potassium cyanate being formed.

$$C_2N_2 + 2\,KOH = KCN + KCNO + H_2O.$$

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[267] *Chem. News,* **87**, 173 (1903).

Determination of Cyanogen.—Cyanogen may be determined by the method of Nauss.[268] 100 liters of the gas mixture is passed at a rate of from 50 to 100 liters per hour through two absorption bottles in each of which is placed 20 cc. of a solution of ferrous sulphate (1:10) and 20 cc. of a solution of potassium hydroxide (1:3). After the passage of the gas, the contents of the absorption bottles is carefully rinsed into a 500 cc. flask, some potassium hydroxide in solution is added and then ferrous sulphate (1:10). If hydrogen sulphide is present, the solution of ferrous sulphate should be added until no further precipitation of black ferrous sulphide results. It is advisable to add also about one gram of lead carbonate to ensure the complete removal of hydrogen sulphide. The contents of the flask is then heated for some minutes and allowed to cool. The flask is filled to the mark, and 5 cc. more of water is added to compensate for the volume of the precipitate. After being vigorously shaken, the liquid is filtered off through a dry paper; 50 cc. of the filtrate is poured into an excess (20 to 30 cc.) of a hot solution of ferric alum that contains 200 grams of ferric alum per liter. The solution is warmed for a short time on a water-bath and Prussian blue is then precipitated by the addition of dilute sulphuric acid. The precipitate is collected on a folded filter in a hot-water funnel, and is washed with hot water until sulphuric acid has been completely removed. The precipitate with the filter is then at once placed in a flask, some water is added, and the liquid is heated to boiling, the contents of the flask being frequently shaken to loosen the precipitate from the paper. The amount of the Prussian blue is then directly determined by titration with a 0.02 *N* solution of sodium hydroxide.

$$Fe_4(Fe(CN)_6)_3 + 12\,NaOH = 4\,Fe(OH)_3 + 3\,Na_4\,Fe(CN)_6.$$

The solution of sodium hydroxide is added, a little at a time, until all of the Prussian blue is decomposed. The contents of the flask is kept hot during the addition of the sodium hydroxide for the purpose of hastening the reaction. The excess of sodium hydroxide is then ascertained by titrating back with 0.02 *N* acid. The liquid must be continuously heated and frequently shaken during this last titration, for even in the presence of an excess of sodium hydroxide there is some re-formation of Prussian blue which causes a green coloration of the liquid. When the color changes to a light greenish yellow, the end point has been reached.

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[268] *J. Gasbel.*, **43**, 696 (1900).

1 cc. 0.02 *N* sodium hydroxide = 0.0007794 gram cyanogen.

Nauss found from 6 to 15 grams of cyanogen in 100 cubic meters of Karlsruhe gas after the last purifier.

Samtleben, using the analytical method of Nauss, found [269] in coal gas of Bernburg from 155 to 301 grams of hydrogen cyanide in 100 cubic meters before the purifiers, and from 8.8 to 21.3 grams per 100 cubic meters after the purifiers.

After the absorption of the cyanogen in the solution of caustic potash containing freshly precipitated ferrous hydroxide in suspension, several methods besides the one described above may be employed for the determination of cyanogen. Feld [270] converts the soluble ferrocyanide into mercuric cyanide, from which the hydrogen cyanide is recovered by distillation with sulphuric or hydrochloric acid. The hydrogen cyanide is absorbed in sodium hydroxide and the resulting sodium cyanide is determined by adding a little potassium iodide and titrating with 0.1 *N* silver nitrate until a permanent yellow precipitate of silver iodide is formed. This method has also been used by Skirrow [271] and Colmann [272] in the analysis of ferrocyanides.

Mueller [273] filters the solution and determines the potassium ferrocyanide in the filtrate by acidifying and titrating with a standard solution of zinc sulphate until all of the ferro-

[269] *J. Gasbel.*, **49**, 205 (1906).

[270] *J. Gasbel.*, **46**, 561 (1903); *J. Soc. Chem. Ind.*, **22**, 1068 (1903).

[271] *J. Soc. Chem. Ind.*, **29**, 319 (1910).

[272] *Analyst*, **35**, 295 (1910).

[273] *Proc. Am. Gas. Inst.*, **5**, 249 (1910).

cyanide has been precipitated as zinc ferrocyanide. This is ascertained by testing a drop of the solution on a filter paper with a one per cent solution of ferric chloride. Drehschmidt[274] removes hydrogen sulphide with mercuric oxide, and then adds an excess of an acidified solution of 0.1 *N* silver nitrate, and titrates the excess with 0.1 *N* solution of ammonium thiocyanate.

Detection and Determination of Cyanogen in Presence of Hydrogen Cyanide.—Wallis[275] observed that when hydrogen cyanide is passed into an acidified solution of silver nitrate it reacts quantitatively with the silver nitrate to precipitate silver cyanide. He also states that cyanogen does not react with an acidified solution of silver nitrate, and that any cyanogen that dissolves as such in the reagent may be removed practically completely by passing a current of air through the solution. Upon this difference of behavior of cyanogen and hydrogen cyanide toward silver nitrate, Wallis bases a method for the detection of cyanogen and of hydrogen cyanide when these gases are present together in a gas mixture, but he carried the work no further than to show the applicability of this method to the qualitative examination of a few special gas mixtures.

Rhodes has made a careful study of the reaction noted by Wallis and has developed a method[276] that permits both of the detection and of the accurate determination of cyanogen in the presence of hydrogen cyanide. For the detection of cyanogen in the presence of hydrogen cyanide he proceeds as follows:

Test tubes 15 cm. long and provided with side arms are used for the absorption of the gases. In one such tube is placed 10 cc. of a 10 per cent solution of silver nitrate to which one drop of dilute (6 *N*) nitric acid has been added. In the second tube is placed 10 cc. of a 2 *N* solution of potassium hydroxide. The two absorption tubes are connected in series and the gas mixture is passed through them. The duration of the passage of the gas depends upon the amount of hydrogen cyanide in the gas mixture. Since the first tube is intended to hold back the hydrogen cyanide, the passage of the gas must of course be stopped before all of the silver nitrate in this tube is converted into silver cyanide. After the gas mixture has been passed through the absorption tubes for a sufficient length of time, it is replaced by a current of air which is continued for about ten minutes. The second absorption tube, which contains the solution of potassium hydroxide, is then disconnected and 5 cc. of a solution of ferrous sulphate and one drop of a solution of ferric chloride are added to the contents of the tube. After about fifteen minutes there is added dilute sulphuric acid in amount sufficient to dissolve the ferrous and ferric hydroxides. The appearance of a blue precipitate or of a distinct green color in the solution after acidification proves the presence of cyanogen in the original gas mixture.

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[274] *J. Gasbel.*, **35**, 268 (1892).

[275] *Ann.*, **345**, 353 (1906).

[276] *Ind. Eng. Chem.*, **4**, 652 (1912).

From the above data it appears that as small an amount as 0.3 cc. of cyanogen may be detected in this manner. That the presence of hydrogen cyanide in the gas does not interfere with the delicacy of this method was demonstrated by passing through the absorbents a mixture of 0.4 cc. of cyanogen and 10 cc. of hydrogen cyanide and obtaining a distinct reaction for cyanogen under these conditions. Even when 20 liters of air were passed through the apparatus subsequent to the introduction of the cyanogen, 0.4 cc. of cyanogen still gave a distinct reaction.

Carbon dioxide in the gas mixture under examination does not interfere with the test for cyanogen unless there is an amount present sufficient to convert all of the potassium hydroxide into potassium carbonate.

The presence of hydrogen cyanide in the original gas mixture is detected by collecting on a filter any precipitate that may have formed in the solution of silver nitrate in the first absorption tube, washing the precipitate with very dilute nitric acid, drying it, transferring it to a small sublimation tube, and warming it with a small amount, five milligrams or less, of iodine. The formation of a sublimate of cyanogen iodide on the side of the tube proves the presence of silver cyanide in the precipitate and consequently of hydrogen cyanide in the original gas mixture; 0.1 mg. of silver cyanide, equivalent to 0.02 mg. of hydrogen cyanide, may be detected in this manner.

To determine cyanogen and hydrogen cyanide in the presence of each other the gas mixture is passed through a series of four absorption test tubes. Each of the first two of these tubes contain 5 cc. of a standard 0.1 *N* solution of silver nitrate and one drop of dilute nitric acid. In the third absorption tube is placed 10 cc. of an approximately 2 *N* solution of potassium hydroxide that is free from chloride, and the last tube contains 5 cc. of this solution. The gas mixture under examination is slowly passed through this absorption apparatus or is carried through by a slow current of air. The first two absorption tubes are then disconnected and the solution of silver nitrate that they contain is transferred to a beaker and is filtered. The precipitate and filter paper are washed with very dilute nitric acid until free from soluble silver salts. The filtrate and wash water are then combined and are titrated with a standardized solution of ammonium thiocyanate with ammonium ferric alum as indicator, and the amount of hydrogen cyanide that was present in the original gas mixture is calculated from the volume of ammonium thiocyanate used.

The contents of the third and fourth absorption tubes is transferred to a beaker and a known volume of a standardized solution of silver nitrate is added. The silver nitrate must be in excess of the amount required to precipitate all of the potassium cyanide in the solution as silver cyanide. The solution and the suspended precipitate are then thoroughly stirred, and dilute nitric acid is next added until the precipitated silver oxide redissolves and the solution becomes slightly acid. The precipitate of silver cyanide is now filtered off, the precipitate and filter paper are washed with very dilute nitric acid until all soluble silver salts are removed, and the filtrate and wash water are combined and are titrated with a standardized solution of ammonium thiocyanate with ammonium ferric alum as indicator. The cyanogen present in the original gas mixture is then calculated, the reactions involved in the calculation being:

$$(CN)_2 + 2\,KOH = KCN + KCNO + H_2O$$

$$KCN + AgNO_3 = AgCN + KNO_3$$

$$AgNO_3 + KCNS = AgCNS + KNO_3$$

HYDROGEN CYANIDE (HCN)

Properties of Hydrogen Cyanide.—Specific gravity (air = 1), 0.9359; density at 0°, 760 mm., 1.2096 grams per liter; boiling point, 26°; melting point, — 14°.

The gas is easily soluble in water and in alcohol, and is absorbed by potassium hydroxide with the formation of potassium cyanide.

Strong acids, especially hydrochloric acid and sulphuric acid, decompose hydrocyanic acid with formation of formic acid and ammonia.

Detection of Hydrogen Cyanide.—Hydrogen cyanide may be detected by absorbing the gas in a solution of potassium hydroxide, and then adding ferrous sulphate and one drop of ferric chloride to the solution of potassium cyanide. If the solution that is being tested is not alkaline, potassium hydroxide should be added at this point. The solution is then gently warmed and is acidified with hydrochloric acid. A dark blue precipitate of Prussian blue proves the presence of potassium cyanide in the absorbent. Since cyanogen is absorbed by potassium hydroxide with the formation of potassium cyanide, that gas will also give this reaction.

Another test for hydrogen cyanide is to add ammonium sulphide until the solution takes on a yellow color, then to add ammonia,—or, better, a drop of sodium hydroxide,—and to heat the solution until the excess of ammonium sulphide has been driven off, and the solution is again colorless. In this way there is formed either ammonium or sodium thiocyanate, which, after acidifying, gives the characteristic blood-red color with ferric chloride.

Hydrogen cyanide may also be detected by the methods proposed by Kunz-Krause and by Schaer which have already been described under Cyanogen.

Grubbs[277] has suggested the use of small animals for the detection of hydrogen cyanide.

Katz and Longfellow[278] have devised for the detection of hydrogen cyanide three papers, one containing sodium picrate, the second guaiacum and copper solution, and the third phenolphthalein and copper solution. The first reagent is yellow and varies from orange to brown with increasing hydrogen cyanide content. The second develops a blue color and the third a pink or bluish pink shade.

Detection of Hydrogen Cyanide in Air.—Sieverts and Hermsdorf[279] state that when a strip of filter paper is freshly moistened with a solution of copper benzidine acetate and is exposed to the air for exactly seven seconds, the depth of the blue color produced indicates roughly the amount of hydrogen cyanide present. Ammonia and cyanic acid do not interfere with the test but oxidizing gases will do so. The solutions of copper acetate (2.86 grams per liter) and benzidine acetate (475 cc. of a cold saturated solution diluted to 1 liter) are prepared separately, protected from the light, and mixed in equal proportions just before use.

Moir[280] uses a filter paper moistened with a reagent consisting of 1 gram of *o*-tolidine, 1.5 grams of copper acetate, 0.5 gram of glacial acetic acid, and 100 cc. of water. A blue color will appear if the air contains one part of hydrogen cyanide in two million parts.

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[277] *Public Health Reports,* **32**, 565 (1917).

[278] *Chem. Abstr.,* **17**, 2686 (1923).

[279] *Z. angew. Chem.,* **34**, 3 (1921); see also Petusi and Gastaldi, *Chem. Ztg.,* **37**, 609 (1913).

[280] *J. So. African Assoc. Anal. Chem.,* **3**, 16 (1920).

Determination of Hydrogen Cyanide.—For the determination of hydrogen cyanide in a gas mixture the method of Andrews[281] may be used. The gas is absorbed in potassium hydroxide and if the resulting solution contains more than about one per cent of hydrogen cyanide, it is diluted with water until its concentration does not exceed one per cent. Two drops of a saturated solution of pure paranitrophenol are then added. If the solution takes on a yellow color, decinormal hydrochloric acid is added until the color has very nearly disappeared. On the other hand, if the solution remains colorless, a decinormal solution of potassium hydroxide is added until a very pale-yellow tint is observed. 15 to 20 cc. of a solution of mercuric chloride containing 40 grams of the pure recrystallized salt per liter is then added, and the solution is stirred and is allowed to stand for one hour at the temperature of the air. The hydrochloric acid set free in the reaction

$$HgCl_2 + 2\,HCN = Hg(CN)_2 + 2\,HCl$$

is then titrated with a decinormal solution of potassium hydroxide, the end point of the titration being shown by the appearance of a pale-yellow tint in the solution.

Powell[282] passes the gas to be tested at the rate of 3 cu. ft. per hour through four wash-bottles, each containing 100 cc. of a 15 per cent solution of sodium hydroxide. At least 20 cu. ft. of gas are used for each 5 grams of hydrogen cyanide per 100 cu. ft. The combined solutions are made up to 500 cc., and 50 cc. is taken for analysis. Precipitated lead carbonate is added and the solution is filtered to free it from sulphur. The filtrate is titrated with a 0.1 *N* solution of silver nitrate, adding a few drops of a 10 per cent solution of potassium iodide to aid in determining the end-point.

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[281] *Am. Chem. J.*, **30**, 187 (1903).

[282] *Am. Gas Assoc. Monthly*, **4**, 621 (1922).

HYDROGEN SULPHIDE (H_2S)

Properties of Hydrogen Sulphide.—Specific gravity (air = 1), 1.1773; density at 0°, 760 mm., 1.5392 grams per liter; critical temperature, 100.4°; critical pressure, 89 atmospheres; boiling point, — 60.2°; melting point, — 82.9°. According to Winkler, one volume of water absorbs at 760 mm. and

0°, 4.670 volumes
5°, 3.977 "
10°, 3.399 "
15°, 2.945 "
20°, 2.582 "
25°, 2.282 "
30°, 2.037 "

One and a half volumes of oxygen are necessary for the combustion of one volume of hydrogen sulphide, and one volume of sulphur dioxide is formed.

$$2\ H_2S + 3\ O_2 = 2\ H_2O + 2\ SO_2.$$

Potassium hydroxide and solutions of salts of several other metals absorb hydrogen sulphide with the formation of sulphides of the metals.

Detection of Hydrogen Sulphide.—If hydrogen sulphide is present in very small amount, its presence is disclosed by its odor,[283] but when the concentration exceeds 0.01 per cent, the characteristic smell becomes less distinctive and irritation of the eyes is produced. It may more certainly[284] be detected by exposing to the gas a strip of white paper moistened with a colorless solution of lead acetate. McBride and Edwards[285] have made a careful study of this test and recommend a simple apparatus and procedure for making it. If hydrogen sulphide is present in the gas mixture, the paper becomes covered with a glistening brownish black layer of lead sulphide.

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[283] Foster and Haldane, *The Investigation of Mine Air* (1905), p. 123.
[284] Wilmet, *Compt. rend.*, **184**, 287 (1927).
[285] *Bureau of Standards, Tech. Paper* No. 41 (1914).

Another method for the detection of hydrogen sulphide is that devised by Ganassini.[286] It is based upon the fact that when ammonium molybdate is reduced by hydrogen sulphide, the molybdenum salt will react with potassium thiocyanate to form molybdenum thiocyanate which when dissolved in water yields a solution of pinkish red color. The reagent is prepared by dissolving 1.25 grams of ammonium molybdate in 50 cc. of water and 2.5 grams of potassium thiocyanate in 45 cc. of water, mixing these two solutions and acidifying with 5 cc. of concentrated hydrochloric acid. The solution is said to be stable for some days if kept in a stoppered bottle and protected from the light. To test for the presence of hydrogen sulphide in the gas mixture the inside of a small porcelain evaporator is moistened with the reagent, and the gas under examination is caused to impinge upon the moistened surface. The test may also be made by dipping a piece of filter paper into the reagent and holding the moistened paper in the gas. If hydrogen sulphide is present, the liquid or the paper takes on a color that varies from a pale pink to a deep pinkish red according to the amount of hydrogen sulphide in the gas. Neither acetylene nor sulphur dioxide produces the red coloration.

Determination of Hydrogen Sulphide.—Hydrogen sulphide may quantitatively be determined by Dupasquier's method,[287] a measured quantity of gas being drawn through a solution of iodine in potassium iodide, to which some starch paste has been added. The operation is stopped as soon as the solution becomes colorless. The reaction is

$$H_2S + 2\,I = 2\,HI + S,$$

but the reaction follows this equation precisely only when the solutions are very dilute and are protected from direct sunlight.

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[286] *Boll. chim. farm.*, **41**, 417 (1902).

[287] Sommerville, *J. Gas Lighting*, **112**, 28 (1910).

This method may also give high results, since unsaturated hydrocarbons and hydrogen cyanide tend to combine with iodine. The determination may be carried out in a Bunte[288] burette, or in the apparatus described by Tutweiler.[289] The hydrogen sulphide may also be absorbed by a standard solution of iodine, and the excess titrated with either sodium thiosulphate or sodium arsenite.[290] Beau[291] absorbs the hydrogen sulphide in caustic soda, adds barium chloride, acidifies and titrates with a standard solution of iodine.

Harding and Johnson[292] have described an apparatus for this determination in which the hydrogen sulphide is absorbed by a solution of cadmium chloride. The hydrogen sulphide is then liberated in a partial vacuum by means of hydrochloric acid, and is titrated with a standard solution of iodine. This same principle has also been used by Way[293] and by Jordan and Fulweiler.[294]

Fresenius[295] determined hydrogen sulphide gravimetrically by first drying the gases with calcium chloride and then absorbing the hydrogen sulphide in U-tubes that are filled with pumice-stone impregnated with copper sulphate. The pumice-stone is prepared as follows: Place 60 grams of pumice-stone, in pieces the size of a pea, in a small porcelain dish, and pour a hot concentrated solution of from 30 to 35 grams of copper sulphate over it. Evaporate the solution to dryness with constant stirring, place the dish in an air- or oil-bath, whose temperature is kept between 150° and 160° C., and let it remain there four hours. A tube containing 14 grams of this copper sulphate pumice-stone takes up about

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[288] Bunte, *J. Gasbel.*, **31**, 899 (1888); Kast and Behrend, *ibid.*, **32**, 159 (1889).

[289] *J. Am. Chem. Soc.*, **23**, 173 (1901).

[290] Czako, *J. Gasbel.*, **62**, 483 (1919); Stone and Wug, *Gas Age-Record*, **51**, 549, 655 (1923); Hegel, *Z. angew. Chem.*, **39**, 431 (1926).

[291] *Am. Gas Assoc. Monthly*, **2**, 265 (1920).

[292] *Ind. Eng. Chem.*, **5**, 836 (1913).

[293] *J. Gas Lighting*, **128**, 660 (1915).

[294] *Chem. Abst.*, **16**, 329 (1922).

[295] Fresenius, *Anleitung zur quant. Analyse*, 6th ed., Part I, p. 505. Also *Z. anal. Chem.*, **10**, 75 (1871).

2 grams of hydrogen sulphide. To make sure of complete absorption two such tubes should always be used.

Wright[296] prefers copper phosphate as an absorbent. It is prepared by adding, with constant stirring, a solution of 100 grams of secondary sodium phosphate (Na_2HPO_4) in 500 cc. of water to a solution of 125 grams of crystalline copper sulphate in 750 cc. of water. The precipitated copper phosphate is washed by decantation, and is dried at 100°.

The U-tube is filled to five-sixths of its length with either absorbent and one-sixth at the exit end with calcium chloride. The increase in weight of the U-tube gives the weight of hydrogen sulphide in the volume of gas used in the test.

Harcourt (see p. 283) has devised a colorimetric method which may be used for the determination of small quantities of hydrogen sulphide. The gas is bubbled through a solution of lead acetate in an excess of sodium hydroxide to which sugar has been added. The gas is passed until the solution has the same brown color as a standard tube of the same size, and from the volume of gas used the amount of hydrogen suphide present may be determined. Clark[297] describes a colorimetric method based on the reaction with iodine. The hydrogen sulphide is absorbed by a solution of iodine containing starch, and then a 0.002 *N* solution of iodine is added until the original color reappears, this being determined by comparison with a standard.

CARBON DISULPHIDE (CS_2)

Properties of Carbon Disulphide.—Specific gravity (water = 1) $^{22}_{20}$ = 1.261; boiling point, 46.3°; melting point, —111.6°.

Detection of Carbon Disulphide.—Carbon disulphide may be detected, according to Vogel,[298] by passing the gas, after drying by calcium chloride, through a solution of potassium hydroxide in absolute alcohol, which results in the formation of potassium xanthate.

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[296] *J. Soc. Chem. Ind.*, **4**, 665 (1885).

[297] *A Study of the Contamination of the Atmosphere with Hydrogen Sulphide in Sections of the Texas Panhandle*, Thesis, Southwestern University (1927).

[298] *Ann.*, **86**, 369 (1853).

$$CS_2 + KOH + C_2H_5OH = C_3H_5OS_2K + H_2O.$$

If this solution is then acidified with acetic acid and is treated with a solution of cupric sulphate, a yellow precipitate of cuprous xanthate is formed. It may also be detected by passing the gas, after drying over calcium chloride, through a dilute solution of triethyl phosphine in ether, which results in the formation of a bright red solution or crystalline compound,

$$P(C_2H_5)_3 + CS_2 = P(C_2H_5)_3 \cdot CS_2.$$

Determination of Carbon Disulphide.—The formation of xanthate mentioned above may also be used for the quantitative determination of carbon disulphide. Macagno[299] titrated the potassium xanthate with a standard solution of cupric sulphate. Harding and Doran[300] found that the method was more satisfactory if the gas were first passed through a solution of caustic potash to remove carbon dioxide, next dried with sulphuric acid, and then run into a solution of potassium hydroxide in alcohol. The solution is acidified with acetic acid, precipitated with an excess of a standard solution of cupric acetate, the precipitate filtered off, and the excess of copper is determined by the addition of potassium iodide and titration with a standard solution of sodium thiosulphate. Huff[301] has modified this procedure so as to be able to detect and determine traces of carbon disulphide in small volumes of gas. The determination might also be made by boiling the alkaline xanthate solution with hydrogen peroxide and determining the sulphate that is formed as barium sulphate.

Hegel[302] states that the method indicated by Hofmann[303] may also be employed. To remove water, the gas mixture is passed over calcium chloride that is heated to 50°, and then through two wash-bottles, each containing 45 cc. of a one per cent solution of triethyl phosphine in dry, fat-free ether cooled to about —10°. A red, crystalline compound is formed which can be filtered off on a Gooch crucible, dried in a vacuum at room temperature for one hour, and weighed. The hydrogen sulphide may be determined in the gas freed from carbon disulphide, by passing it through a standard solution of iodine and titrating the excess with sodium thiosulphate.

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[299] *Chem. News*, **43**, 138 (1881).
[300] *J. Amer. Chem. Soc.*, **29**, 1480 (1907).
[301] *J. Amer. Chem. Soc.*, **48**, 81 (1926).
[302] *Z. angew. Chem.*, **39**, 431 (1926).
[303] *Ber.*, **13**, 1732 (1880).

Carbon disulphide may also be determined by converting it to hydrogen sulphide by passing it over heated platinized pumice and determining this colorimetrically by Harcourt's method. A 30 cc. fractionating flask is filled with platinized pumice and is surrounded by a glass chimney. The bottom of the flask is about 2.5 cm. above a ring burner at the bottom of the chimney. The flame of the burner is so adjusted as to heat the pumice to 300 to 350° C., and the gas is passed through at about 0.5 cu. ft. per hour. After about ten minutes the tube containing lead acetate (see p. 281) is connected, and the gas is drawn through with the aspirator until the color is the same as the standard. Then from the volume of gas that has been aspirated, the amount of carbon disulphide may be calculated. This method gives results of fair accuracy only when the gas is free from oxygen.

The separate determination of carbon disulphide, however, is not often made, since all of the information desired can be obtained by the determination of total sulphur (p. 350).

SULPHUR DIOXIDE (SO_2)

Properties of Sulphur Dioxide.—Specific gravity (air = 1), 2.2639; density at 0°, 760 mm., 2.9267 grams per liter; critical temperature, 157.2°; critical pressure, 77.7 atmospheres; boiling point, —10°; melting point, —72.7°.

Sulphur dioxide is easily soluble in water. According to

Sims,[304] one volume of water dissolves at 760 mm. and at

8°, 58.7 vol. SO_2
10°, 53.9 “ “
14°, 45.6 “ “
20°, 36.4 “ “
24°, 32.3 “ “
30°, 27.3 “ “

The gas reddens moist blue litmus paper and is readily absorbed by solutions of the hydroxides of the alkali metals. If carbon dioxide is absent, sulphur dioxide may be determined by absorption with sodium hydroxide. If both gases are present, the amount of sulphur dioxide may be ascertained by titration. It may also be determined either by leading a measured volume of the gas through a solution of bromine in water, and precipitating the sulphuric acid thus formed by barium chloride, or by measuring the amount of gas required to decolorize an iodine solution of known strength.

This latter method has been very generally employed for the determination of sulphur dioxide in “burner gas,” the usual procedure being that recommended by Reich.[305] The operation may be carried out in the apparatus described on page 21. 10 cc. of a standard solution of iodine containing 12.962 grams of iodine per liter is diluted with water, some starch solution is added, and the reagent is placed in a Friedrichs spiral gas washing-bottle. The gases are drawn through the iodine solution by means of an aspirator until the liquid is decolorized, and the volume of water that has run from the bottle into a graduated cylinder is measured.

The reaction proceeds according to the equation:

$$SO_2 + I_2 + 2\ H_2O = H_2SO_4 + 2\ HI.$$

The amount of sulphur dioxide in the mixture under examination may then be calculated as follows: One cc. of the standard iodine solution corresponds to 0.0032 gram SO_2 which amount under standard conditions possesses a volume of 1.118 cc. If b equals the prevailing barometric pressure, t the temperature, h the difference in height in millimeters between the level of the water in the bottle and the lower end of the siphon tube, and n the cubic centimeters of iodine solution employed, then the actual volume under the prevailing conditions of the sulphur dioxide, s, that has passed through the iodine solution, may be calculated by use of the following formula:

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[304] *J. Chem. Soc.*, **14**, 1 (1862).
[305] *Berg-und Hüttenmänn, Zeit.*, 1858.

$$s = 1.118 \times n \times \frac{760}{b - \frac{h}{13.6}} \times (1 + 0.00367\,t) \text{ cc.}$$

The volume of the water, w, in the graduated cylinder is equal to the amount of gas that has been drawn through the iodine solution exclusive of the volume of sulphur dioxide; consequently the total volume of gas equals w + s and the per cent of sulphur dioxide in the gas mixture equals

$$\frac{100 \times s}{w + s}.$$

If it should not be deemed necessary to introduce corrections for the pressure and temperature, the formula becomes

$$\frac{111.8 \times n}{w + 1.118 \times n} = \text{per cent } SO_2.$$

If 10 cubic centimeters of the standard (decinormal) iodine solution is used, the volume percentage of sulphur dioxide in the original gas mixture that is indicated by different volumes of water collected in the graduated cylinder is shown in the following table.

An apparatus that is based upon the same principle as that of Reich, but which is so constructed that the per cent of

TABLE XIV [306]

Cubic Centimeters Water Collected.	Volume Per Cent SO_2 in Kiln Gas
82	12
86	11.5
90	11
95	10.5
100	10
106	9.5
113	9
120	8.5
128	8
138	7.5
148	7
160	6.5
175	6
192	5.5
212	5

sulphur dioxide in the gas mixture may be directly read off, has been described by Kreidl.[307]

The method of Reich cannot be used for the determination of sulphur dioxide in the gases from the lead chambers of the sulphuric acid process because the hydriodic acid that is formed is quickly oxidized again to iodine by the nitrous acid that is present. The iodine that is thus set free then oxidizes additional amounts of sulphur dioxide with the result that the percentage of sulphur dioxide in the gas mixture appears to be much smaller than it actually is. Moreover, the presence of nitrous acid renders the end-point of the reaction, the decolorization of the iodine solution, uncertain for the reason that after decolorization has been effected by the sulphur dioxide the blue color reappears because of the action of the nitrous acid. For the determination of sulphur dioxide in the presence of nitrous acid, it is consequently necessary to modify the method in such manner as to prevent the interference of nitrous acid, and this is accomplished by

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[306] Lunge, *Sulphuric Acid and Alkali*, Vol. 1, Part 1, p. 415 (1903).
[307] *Z. f. Zuck.-Ind.*, Böhm., **24**, 658 (1900).

Raschig[308] by adding sodium acetate to the solution. This reacts with the free nitrous acid to form sodium nitrite, and under these conditions the iodine is decolorized solely by the sulphur dioxide.

The nitrous acid in the gases may then be determined by rinsing out the contents of the absorption bottle into a flask, adding a drop of phenolphthalein, and titrating the free acetic acid with a decinormal solution of sodium hydroxide. From the volume of the sodium hydroxide solution used, there is to be subtracted 10 cc. for the hydriodic acid resulting from the reduction of the 10 cc. of decinormal iodine solution, and also 10 cc. more for the sulphuric acid formed in the reaction (see page 284). The balance of the sodium hydroxide that is used indicates free nitric acid or nitrous acid. Raschig states that while the method gives satisfactory results for sulphur dioxide, it is not very exact for the determination of the oxides of nitrogen if the gas sample is taken from the beginning of the lead chambers, because here the sulphur dioxide is present in preponderating amount. If, however, the gas sample is taken from the end of the chamber system where the oxides of nitrogen are present in much larger proportion, a proportionately larger sample of the gases will be needed to decolorize the iodine solution and a determination of the oxides of nitrogen will be correspondingly more exact.

For the determination of minute amounts of sulphur dioxide in air, Seidell and Menserve[309] have shown that with 2½ liter samples, direct titration with 0.001 N solution of iodine may be employed. A correction factor of 1.3 must be applied for the apparent incompleteness of the reaction at the great dilution; on account of the gradual oxidation of the sulphur dioxide, which is hastened by the presence of moisture, the titrations must be made immediately after the collection of the sample.

The determination of sulphur dioxide by titration with iodine has been studied by the Shelby Commission.[310] The sulphur dioxide is absorbed by 0.002 *N* solution of iodine containing some starch: a standard solution of iodine is then added until the blue color matches that of the "blank" determination. By means of partially evacuated bottles the use of water in sampling is eliminated, and in the "blank" determination, attention is paid to the errors that may arise from moisture, the action of iodine on rubber, and the influence of light, temperature, or time on the color of the starch iodine solutions.

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[308] *Z. angew. Chem.*, **22**, 1182 (1909).

[309] *Ind. Eng. Chem.*, **6**, 298 (1914).

[310] *U. S. Bureau of Mines, Bulletin* 98 (1915), p. 200.

Sweeney, Outcault and Withrow[311] state that the above method is open to objection because it uses a solution of iodine which must frequently be standardized, and is so sensitive to the action of light that a "blank" determination must be made. To overcome this difficulty they use a solution of potassium permanganate instead of iodine.

In a critical review of the various idometric methods now used, Ferguson[312] recommends for general work with gaseous mixtures containing sulphur dioxide the method of bubbling the sample through an excess of a solution of iodine in an all-glass apparatus, allowing the gas to stand over the iodine, and then titrating the excess with a solution of sodium thiosulphate. Oxidation of the sulphur dioxide-air mixtures does not take place to an appreciable extent if the gases are kept absolutely dry.

Lowe[313] uses a solution of sodium iodide and iodate to absorb the sulphur dioxide, and after the passage of a measured volume of the gas mixture, the solution is acidified and titrated with a solution of sodium thiosulphate.

As stated above, sodium hydroxide is often employed for the determination of total acid gases. Lunge[314] recommends the determination of sulphur dioxide and sulphur trioxide by passing them through a solution of sodium hydroxide containing phenolphthalein, until the pink color disappears. The phenolphthalein indicates the simultaneous formation of sodium sulphite and sodium sulphate from these gases. When the test is prolonged, oxidation of the sodium sulphite occurs, and Titoff[315] has shown that the rate of oxidation is influenced by the presence of small amounts of catalysts. This may be prevented by the addition of a negative catalyst, and Haller[316] has suggested the addition of about five per cent by volume of glycerin to the sodium hydroxide. The sulphite formed is then titrated with potassium iodate in acid solution.

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[311] *Ind. Eng. Chem.*, **9**, 949 (1917); *J. Soc. Chem. Ind.*, **36**, 1233 (1917).

[312] *J. Amer. Chem. Soc.*, **39**, 364 (1917).

[313] *J. Soc. Chem. Ind.*, **40**, 163 (1921).

[314] *Z. angew. Chem.*, **3**, 563 (1890).

Dieckmann[317] recommends passing the gas mixture through sodium hydroxide containing phenolphthalein and methyl orange. The first color change, red to yellow, gives the volume per cent of sulphur dioxide and sulphur trioxide. The passage of the gas is continued until the sodium hydroxide is neutralized, the difference in the two readings giving the sulphur dioxide. Berl[318] states that under such conditions, if the gas contains both oxygen and sulphur dioxide, some of the sulphur dioxide is oxidized to sulphate. He investigated many different catalysts to prevent this, and advocates the use of an absorbent solution containing 0.23 gm. of $SnCl_2 \cdot 2\ H_2O$ per liter.

Sander[319] recommends aspirating the gas mixture through a solution of sodium hydroxide containing methyl orange. The color change from yellow to pink indicates the formation of primary sodium sulphite and sodium sulphate from the sulphur dioxide and sulphur trioxide. The neutral solution is transferred to a flask and is treated with a solution of mercuric chloride,

$$NaHSO_3 + HgCl_2 = HgCl \cdot NaSO_3 + HCl.$$

The liberated acid is titrated with sodium hydroxide which gives the sulphur dioxide content. This method has been criticised by Stuer and Grob.[320]

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[315] *Z. physik. Chem.*, **45**, 641 (1903).

[316] *J. Soc. Chem. Ind.*, **38**, 52 (1919).

[317] *Papierfabr.*, **19**, 285 (1921); *Chem. Ztg.*, **45**, 885 (1921).

[318] *Chem. Ztg.*, **45**, 693 (1921).

[319] *Chem. Ztg.*, **45**, 261, 554 (1921).

Ries and Clark[321] advocate a method which is a combination of those of Haller and Berl. The sulphur dioxide is absorbed by bubbling the gas mixture through 10 cc. of a ten per cent solution of sodium hydroxide, to which a small amount of stannous chloride (0.002 *M*) has been added. After absorption, the solution is transferred to a flask, diluted to 50 cc., cooled, 50 cc. of 12 *N* hydrochloric acid added, the solution again cooled, and 2 cc. of carbon tetrachloride is added. It is then titrated with 0.003 *M* potassium iodate, the flask being shaken very vigorously during the titration until the pink color of the carbon tetrachloride disappears. The reaction occurring is

$$KIO_3 + 2\,H_2SO_3 + 2\,HCl = 2\,H_2SO_4 + KCl + ICl + H_2O.$$

Lunge has suggested that these gases might be determined by measuring the specific gravity, and Saillard and Bregmann[322] have suggested a conductivity method. Gille[323] has proposed a method for the determination of sulphur trioxide by absorbing it with a 10 cm. plug of cotton, digesting with water and titrating; Schmidt[324] finds that this method is accurate only when the gas is dry.

CARBON OXYSULPHIDE (COS)

Properties of Carbon Oxysulphide.—Specific gravity (air = 1), 2.0752; density at 0°, 760 mm., 2.721 grams per liter; critical temperature, 105°; critical pressure, 65.1 atmospheres; melting point, — 138°; boiling point, — 48°. According to Winkler, one volume of water absorbs at 760 mm. and at

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[320] *Chem. Ztg.*, **45**, 553, 770 (1921).
[321] *Ind. Eng. Chem.*, **18**, 747 (1926).
[322] *Rev. gen. chim.*, **20**, 69 (1918).
[323] *Z. angew. Chem.*, **39**, 401 (1926).
[324] *Z. angew. Chem.*, **39**, 732 (1926).

0°, 1.348 vol.
10°, 0.844 "
20°, 0.568 "
30°, 0.407 "

Pure carbon oxysulphide has no odor, and its freshly prepared solution in water has no taste. Its action upon the nervous system is somewhat similar to that of nitrous oxide.[325] When inhaled for a few seconds it causes dizziness and buzzing in the ears, but if the inhalation is not continued, the symptoms quickly disappear. This gas may sometimes be present in coal-gas.[326]

A solution of potassium hydroxide absorbs carbon oxysulphide very slowly, but the gas is rapidly taken up by a solution prepared by dissolving one part of potassium hydroxide in two parts of water and adding an equal volume of alcohol. A cubic centimeter of this reagent is able to absorb 72 cc. of carbon oxysulphide. The gas is but slightly soluble in a hydrochloric acid solution of cuprous chloride. 1 cc. of this solution absorbs about 0.2 cc. of the gas.

Carbon oxysulphide may be separated from hydrogen sulphide by absorbing the latter in an acidulated solution of copper sulphate. Separation from vapor of carbon disulphide may be effected by passing the gases through a mixture of one part of triethylphosphine and nine parts of chloroform, which absorbs the carbon disulphide. The most delicate reagent for its detection is "iodide of starch." If the gas is passed through a starch solution that is colored a clear blue by a trace of iodine, the color of the solution is very slowly discharged. The blue tint changes first to violet, then to red, and finally the color disappears completely. Other gases that would act upon the iodide of starch must of course be absent.

One volume of carbon oxysulphide needs 1½ volumes of oxygen for its combustion and yields one volume of CO_2 and one volume of SO_2.

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[325] Klason, *J. prakt. Chem.*, **36**, 64 (1887).
[326] *J. Gasbel.*, **52**, 288 (1909).

Determination of Carbon Oxysulphide.—Hempel determines[327] carbon oxysulphide in the presence of hydrogen sulphide and carbon dioxide by first absorbing the hydrogen sulphide with an acid solution of copper sulphate, then decomposing the carbon oxysulphide into carbon monoxide and sulphur by passing the residual gas mixture through a hot capillary tube of platinum, determining the carbon monoxide that is here set free by absorption in a hydrochloric acid solution of cuprous chloride, and finally determining the carbon dioxide by means of potassium hydroxide.

Witzeck[328] raises objections to this method and gives preference to the procedure proposed by Schwartz,[329] which consists in passing the gas mixture through an iodine solution for the removal and the determination of hydrogen sulphide, and then shaking the residual gas with a solution of potassium hydroxide which will decompose the carbon oxysulphide with the formation of potassium sulphide and potassium carbonate. To this solution hydrochloric acid is then added to set free hydrogen sulphide and carbon dioxide. The hydrogen sulphide is determined by means of an iodine solution and the carbon dioxide is determined by absorption with potassium hydroxide. Since one volume of carbon oxysulphide yields upon decomposition one volume of hydrogen sulphide and one volume of carbon dioxide, the amount of carbon dioxide present in the original mixture is ascertained by subtracting from the volume of carbon dioxide formed, a volume equal to that of the hydrogen sulphide found to be present.

Dede[330] states that carbon oxysulphide may be determined in spring gases by passing the gas mixture through a dilute, acidified, solution of palladium dichloride, heated to 50°. The following reaction occurs,

$$COS + PdCl_2 + H_2O = PdS + 2\,HCl + CO_2.$$

The palladium sulphide, and palladium which may be present due to reduction by hydrocarbons, are filtered off, dissolved in hydrochloric acid with the addition of potassium chlorate and the sulphuric acid is determined as barium sulphate.

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[327] *Z. angew. Chem.*, **14**, 865 (1901).
[328] *J. Gasbel.*, **46**, 145 (1903).
[329] *Chem. Ztg.*, **12**, 1018 (1888).
[330] *Chem. Ztg.*, **38**, 1073 (1914).

Stock and Seelig[331] have described two methods for the analysis of mixtures containing carbon monoxide, carbon dioxide, carbon disulphide, and carbon oxysulphide, which depend upon the difference in the rates of absorption of these gases by alkali. In the first method, a measured volume of the gas mixture is shaken with one cc. of a thirty per cent solution of sodium hydroxide, and the volume is read every minute for several minutes. The decrease in volume is the carbon dioxide. Four cc. of water is added and with occasional shaking the volume is read every ten minutes for about one hour. The decrease in volume is the carbon oxysulphide. One cc. of a thirty per cent. solution of caustic potash is added and the volume is recorded every day for several days. The decrease in volume is the carbon disulphide. The residue is carbon monoxide which should be completely absorbed by a solution of cuprous chloride.

In the second method, the carbon dioxide is determined in one portion by shaking with 1 to 2 cc. of a thirty per cent solution of caustic soda. A second portion is shaken occasionally with 2 to 3 cc. of a fifty per cent solution of caustic soda for fifteen to thirty minutes, and is then shaken continuously, the volume being read every minute until constant. This gives the carbon dioxide and carbon oxysulphide. A third portion is shaken with 2 to 3 cc. of a five per cent solution of caustic potash and the volume is determined daily until constant. This gives the carbon dioxide, carbon oxysulphide, and carbon disulphide. The residue is carbon monoxide which should be tested for purity by absorption with cuprous chloride.

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[331] *Ber.*, **52**, 672 (1919).

FLUORINE (F_2)

Determination of Fluorine.—Oettel[332] devised a method for the determination of fluorine in solid compounds, the fluorine being evolved as silicon tetrafluoride, and the volume of this gas then being directly measured. Since a large number of substances contain both fluorine and carbon dioxide, Hempel and Scheffler[333] have modified the method to permit of the simultaneous determination of fluorine and carbon dioxide in a single sample.

The fluorine is set free as silicon tetrafluoride together with carbon dioxide in a suitable apparatus, is collected in a burette, and the silicon tetrafluoride is then decomposed and absorbed by means of water (a small volume of carbon dioxide is here taken up by the water). The carbon dioxide still present in the gas is then completely removed by passing the gas into a pipette containing caustic soda. The gas residue is again brought over the water which was first used and by which the silicon tetrafluoride was absorbed; the absorbed carbon dioxide hereupon escapes from the water and passes into the gas residue. Upon transferring the gas once more to the caustic soda pipette, the remainder of the carbon dioxide is removed, and this volume is subtracted from the diminution first obtained by the absorption with water. The difference gives the amount of silicon tetrafluoride. In this manner it is possible to make very sharp determinations of fluorine in the presence of carbon dioxide.

For setting free the silicon tetrafluoride there is used the apparatus shown in Fig. 75. The evolution flask is connected with a simple gas burette filled with mercury and containing on top of the mercury some concentrated sulphuric acid. It is well to join to the burette a level-bulb instead of a level-tube, and to attach a glass stopcock to the lower end of the burette.

The substance under examination is mixed with finely powdered quartz, the weight of the quartz being fifteen times that of the fluorine which is probably present in the material. The quartz is first heated for a long time in a muffle furnace with free access of air to remove every trace of organic matter.

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[332] *Z. anal. Chem.*, **25**, 505 (1886).

[333] *Z. anorg. Chem.*, **20**, 1 (1899); Sertz, *Z. anal. Chem.*, **60**, 321 (1921).

The sulphuric acid to be employed must be freed from organic substances and from oxides of nitrogen. This is accomplished by adding to concentrated sulphuric acid about 5 grams of powdered sulphur and then fuming down the acid to two-thirds of its original volume.

In carrying out a determination the evolution flask is first carefully dried and the substance, together with the proper amount of quartz powder, is then introduced into the flask by means of a long weighing tube, and the two powders are mixed as intimately as possible by shaking the flask. The flask is then joined by means of the capillary *D* and a piece of dry rubber tubing to the gas burette which contains mercury and some sulphuric acid, as above described. The rubber tube is held firmly in place by means of ligatures of light wire. The volume of concentrated sulphuric acid which is placed in the burette amounts to only about 0.25 cc. Its presence is necessary to avoid the possibility of decomposition of the silicon tetrafluoride by any moisture that might be in the burette.

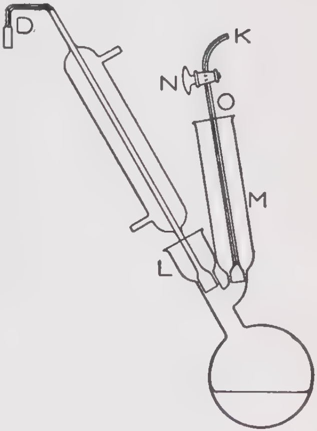

FIG. 75

In the bells *L* and *M* is placed some of the highly concentrated sulphuric acid. A water suction pump is now connected to *K*, and the flask is partially exhausted. The stopcock *N* is then closed, and upon lifting the tube *O* sulphuric acid flows down from *M* into the flask. The flask is shaken so as to bring the acid into intimate contact with the mixture of quartz and the substance, and the contents of the flask is then heated fully up to the boiling-point of sulphuric acid, the heating being continued for about fifteen minutes.

If the apparatus should break, the operator might be seriously injured by the hot concentrated sulphuric acid. It is well, therefore, to protect the eyes with goggles, and to place a glass screen between the flask and the operator.

The heating is now stopped, and the gas in the flask is completely driven over into the burette by filling *M* with concentrated sulphuric acid and carefully lifting the tube *O*. The flask is then disconnected from the burette and the total volume of the gas is measured.

The burette is now connected in the ordinary manner, by means of a capillary tube, with a simple mercury absorption pipette, the pipette containing 5 cc. of water above the mercury. The gas is transferred to the pipette and shaken for five minutes with the water. It is then brought back into the burette and the diminution in volume is read off.

The remaining gas is passed into a pipette filled with a solution of sodium hydroxide to absorb carbon dioxide, and is then drawn back into the gas burette. The volume is observed, and the gas is now passed into the mercury pipette, and shaken again for three minutes. It is then passed back into the burette, and the residual volume of gas is measured. This gas is then passed once more into the sodium hydroxide pipette to determine the small amount of carbon dioxide which was taken up by the water used in the first absorption of the silicon tetrafluoride.

All of these operations can be carried out with considerable speed, and it is therefore easily possible to make a determination of fluorine in two hours.

In determining fluorine in material that contains organic matter, it is very important that the substance should be completely incinerated, since the slightest trace of residual carbon would act upon the boiling sulphuric acid and cause the formation of sulphur dioxide, a gas which would then be absorbed by water when the silicon tetrafluoride is determined.

After absorption in caustic potash, fluorine may be determined gravimetrically.[334] The solution containing the fluorine is neutralized with 0.1 *N* hydrochloric acid and a large excess of a cold, saturated solution of lead chloride is added, precipitating the fluorine as PbFCl. The solution is allowed to stand over night and the precipitate is then filtered off on a Gooch crucible. It is washed first with an almost saturated solution of lead chloride, then three or four times with water, dried at 140° to 150°, and weighed.

CHLORINE (Cl_2)

Properties of Chlorine.—Specific gravity (air = 1), 2.4494; density at 0°, 760 mm., 3.214 grams per liter; critical temperature, 144°; critical pressure, 76 atmospheres; boiling point, —34.6°; melting point, —101.6°.

Chlorine is quite soluble in water. According to Winkler, one volume of water absorbs the following volumes of chlorine:

10°, 3.148
15°, 2.680
20°, 2.299
25°, 2.019
30°, 1.799
35°, 1.602
40°, 1.438

The presence of small quantities of chlorine may be detected by means of the copper flame test.[335]

Determination of Chlorine.—Chlorine may be determined by the Bunsen procedure, in which the gas is led through a solution of potassium iodide, and the iodine set free is titrated with sodium thiosulphate:

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[334] Starck, *Z. anorg. Chem.*, **70**, 173 (1911).

[335] Lamb, Carleton, Hughes and Nichols, *J. Amer. Chem. Soc.*, **42**, 78 (1920).

$$Cl_2 + 2\,KI = 2\,KCl + 2\,I$$

$$2\,Na_2S_2O_3 + 2\,I = Na_2S_4O_6 + 2\,NaI.$$

Chlorine is absorbed by potassium hydroxide or sodium hydroxide. In cold dilute solutions the hypochlorite and chloride of the alkali are formed:

$$2\,KOH + Cl_2 = KClO + KCl + H_2O.$$

In hot concentrated solutions, the reaction is:

$$6\,KOH + 3\,Cl_2 = 5\,KCl + KClO_3 + 3\,H_2O.$$

The first of these two reactions was used by Treadwell in the determination of chlorine in the presence of carbon dioxide, but Offerhaus [336] found that even with a very dilute solution of sodium hydroxide an appreciable amount of sodium chlorate is formed, and that for this reason the titration of the hypochlorite with 0.1 *N* arsenious acid gives results about 0.7 per cent too low. Offerhaus obtained very satisfactory results by passing the mixture of chlorine and carbon dioxide through two dry Bunte burettes connected in series, determining chlorine in the first burette by absorbing the gas with a solution of potassium iodide and titrating the liberated iodine, and in the second burette determining the total amount of chlorine and carbon dioxide by absorption of the two gases with 0.2 *N* sodium hydroxide. The difference between the two results gives the amount of carbon dioxide.

To avoid the use of two gas burettes, Treadwell and Christie [337] absorb the chlorine in a decinormal solution of primary potassium arsenite, KH_2AsO_3, and directly afterward determine the carbon dioxide in the gas mixture by absorption with a solution of potassium hydroxide.

They used a water-jacketed Bunte burette with a tail-stopcock at the bottom as well as at the top, and with the upper part of the burette narrow to render more accurate the reading of small residual gas volumes. The burette is cleaned and thoroughly dried, and the gas mixture is then passed into the burette through the lower stopcock and out through the upper stopcock, the passage of the gas being continued until all of the air that was originally in the burette has been displaced. The lower stopcock is then closed and after ten seconds the upper stopcock is closed, and the barometric pressure and temperature of the water surrounding the burette are noted. The lower stopcock is then turned so that the burette communicates with the tube from the level-bottle. Treadwell and Christie use a level-tube in place of the level-bottle. The level-tube is filled with distilled water and this is allowed to flow through the rubber connecting-tube and out through the end of the lower stopcock to expel air from the tube and chlorine from the end tube and lower stopcock. When the water has flowed out of the level-tube and only the connecting rubber tube is filled with water, the lower stopcock is closed and there is poured into the level-tube exactly 100 cc. of a decinormal solution of primary potassium arsenite. This solution is prepared by dissolving 4.95 grams of arsenic trioxide in a dilute solution of potassium hydroxide, adding phenolphthalein and then sulphuric acid until the color of the solution disappears, and finally diluting to one liter. The lower stopcock is then turned so that the level-tube communicates with the burette. The arsenite solution at first rises rather slowly in the burette, but later its passage is more rapid. Toward the close of the absorption of the chlorine, the burette is shaken to hasten the completion of the reaction.

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[336] *Z. angew. Chem.*, **16**, 1033 (1903).
[337] *Z. angew. Chem.*, **18**, 1930 (1905).

After the absorption of the chlorine has been effected, which takes about 5 minutes, the liquid in the two tubes is brought to the same height and the volume of gas remaining in the burette is read off. The level-tube is now lowered, 10 cc. of a solution of potassium hydroxide (1:2) is poured into the funnel at the top of the burette, the upper stopcock is carefully opened and the solution drawn down into the burette. The stopcock is then closed, the burette is shaken to hasten the absorption of the carbon dioxide, the liquid in the burette and level-tube is brought to the same height and the residual gas volume is read off, the temperature and barometric pressure being again noted.

All of the liquid in the level-tube and in the burette is then transferred to an Erlenmeyer flask and the apparatus thoroughly rinsed with water which is also added to the contents of the flask. Some phenolphthalein is then added to the solution and dilute hydrochloric acid (1:4) is run in until the red color of the liquid just disappears. 60 cc. of a solution sodium bicarbonate containing 40 grams of the salt per liter is then added together with a little starch solution, and the excess of arsenious acid is determined by titration with 0.1 *N* solution of iodine.

In calculating the results, allowance must be made for the fact that the original mixture of chlorine and carbon dioxide is usually practically free from moisture, while the gas residue in the burette is measured in the moist condition. The volume which the residual gas would occupy if dry and at the pressure and temperature under which the gas sample was measured must consequently first be calculated. The difference between this volume and the original volume of the sample in the burette will give the total amount of chlorine and carbon dioxide. The amount of chlorine may be read off after the absorption of that gas by the arsenite solution and the correction of the residual volume, or it may be determined by titration with an iodine solution as above mentioned. One cc. of an 0.1 *N* solution of iodine corresponds to 0.0035457 gram chlorine, and this weight of chlorine under standard conditions will occupy a volume of 1.1015 cc.

Treadwell and Christie state that the determination of chlorine by absorption with the arsenite solution agrees quite closely with the results obtained by titration, the average difference amounting to 0.13 per cent.

If a solution contains free chlorine together with hydrochloric acid, they may both be determined in the following manner (Fresenius):

To a weighed portion of the liquid add an aqueous solution of sulphurous acid until the latter is in excess; after some time add nitric acid and then some potassium chromate to destroy the excess of sulphur dioxide, and precipitate the total chlorine as silver chloride.

If now the amount of free chlorine is determined in a second portion by potassium iodide, the difference gives the quantity of chlorine present in the form of chloride.

The total chlorine may be volumetrically determined by absorbing the gases with a solution of sodium hydroxide, adding sulphur dioxide, then, after a while, nitric acid and some potassium chromate, and finally neutralizing the solution by adding calcium carbonate. All chlorine is now present as chloride, and the solution is neutral, so that the chlorine may be titrated with a neutral solution of silver nitrate, potassium chromate being used as indicator.

Lamb, Carleton and Meldrum[338] determine very small quantities of chlorine with a nephelometer.

HYDROGEN CHLORIDE (HCl)

Properties of Hydrogen Chloride.—Specific gravity (air = 1), 1.2684; density at 0°, 760 mm., 1.6392 grams per liter; critical temperature, 51.4°; critical pressure, 81.5 atmospheres; boiling point, — 85°; melting point, — 111°.

According to Roscoe and Dittmar, one volume of water dissolves at a pressure of 760 mm. the following volumes and weights of hydrogen chloride:

Temperature	Volumes	Grams	Temperature	Volumes	Grams
0	507	0.824	20	442	0.721
4	494	0.804	24	429	0.700
8	481	0.783	28	417	0.682
12	468	0.762	30	412	0.673
16	455	0.742	40	386	0.633

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[338] *J. Amer. Chem. Soc.*, **42**, 251 (1920).

Determination of Hydrogen Chloride.—If no other acid gas is present with the hydrogen chloride, it may be determined by drawing a measured quantity of the gas through a standardized solution of an alkali and titrating back with an acid.

Hydrogen chloride may also be determined by absorbing it with an alkaline solution free from chlorine, and, after acidifying, precipitating it with silver nitrate, and weighing as silver chloride.

A method proposed by Winkler,[339] and based upon Volhard's volumetric method for the determination of silver,[340] consists in placing in a suitable absorption apparatus a few drops of ammonium thiocyanate or potassium thiocyanate, some iron alum solution, and a measured amount of 0.1 *N* silver nitrate solution. Upon leading the gas through this solution the hydrochloric acid reacts with the silver, forming silver chloride. The end of the reaction is shown by the blood-red color. The appearance of this color is due to the fact that after all of the silver nitrate has been changed to silver chloride, the silver thiocyanate present is also decomposed and ferric thiocyanate is formed. The volume of the gas is measured and the amount of hydrogen chloride that it contains is calculated.

PHOSGENE[341] ($COCl_2$)

Properties of Phosgene.—Density at 0°, 760 mm., 1.435 grams per cc.; boiling point, 8.2°; melting point, —126°.

Phosgene is a colorless gas with a peculiar odor. It is decomposed by water according to the equation

$$COCl_2 + H_2O = 2\,HCl + CO_2.$$

It is very soluble in organic solvents such as toluene or xylene.

Detection of Phosgene.—Phosgene may easily be detected by passing it through a cold, saturated, aqueous solution of aniline.[342] After standing two hours, the insoluble diphenylurea which is formed,

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[339] *Anleitung zur Untersuchung der Industrie-Gase,* Part II, p. 322.

[340] *Z. anal. Chem.,* **13,** 171 (1874); **17,** 482 (1878).

[341] Atkinson, Heycock and Pipe, *J. Chem. Soc.,* **117,** 1410 (1920).

$$COCl_2 + 4\,C_6H_5NH_2 = CO(NHC_6H_5)_2 + 2\,C_6H_5NH_2HCl$$

is filtered off and identified by its melting point, 99°. The method will also give fairly accurate quantitative results if the precipitate is washed with cold water, dried at 70°, and weighed.

Determination of Phosgene.—A more accurate method for the determination is to treat the diphenylurea by the Kjeldahl process and then determine the amount of ammonia colorimetrically.[343] If bromine or chlorine is present in the gas mixture, it must first be removed by passing the gas mixture through cotton that has been impregnated with a saturated solution of potassium iodide.

In the absence of hydrogen chloride or chlorine, phosgene may be determined by passing a known volume of the gas mixture (2 to 3 liters) in eight to ten hours through 10 cc. of a 10 *N* solution of sodium hydroxide mixed with 50 cc. of 95 per cent alcohol. After absorption, the solution is evaporated on a water-bath and the sodium chloride is determined in the usual manner.[344]

Reeves[345] has described a rapid method which consists in passing the gas mixture through an excess of strong 13 *N* sodium hydroxide and determining the phosgene both from the excess alkali and from the chlorine formed in the decomposition. By this method the free hydrogen chloride in phosgene may also be determined.

METHYL CHLORIDE (CH_3Cl)

Properties of Methyl Chloride.—Specific gravity (air = 1), 0.9523; density at 0°, 760 mm., 2.3045 grams per liter; critical temperature, 143°; critical pressure, 65.9 atmospheres; boiling point, — 24.09°; melting point, — 91.5°.

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[342] Kling and Schmutz, *Compt. rend.*, **168**, 773 (1919).
[343] Kling and Schmutz, *Compt. rend.*, **168**, 891 (1919).
[344] Dyson, *Chem. Rev.*, **4**, 109 (1927).
[345] *J. Soc. Chem. Ind.*, **43**, 279 (1924).

One volume of water dissolves 5.03 volumes at 7° and 3.46 volumes at 20°. Methyl chloride is quite soluble in alcohol and glacial acetic acid.

Determination of Methyl Chloride.—Allison and Meighan[346] have found that in the absence of components soluble in organic solvents, the absorption of methyl chloride in glacial acetic acid furnishes a simple and fairly accurate method for its determination. The gas mixture containing methyl chloride is measured in a burette and is passed six times into a Hempel pipette containing glacial acetic acid. The residual gas is brought back into the burette and measured, the contraction indicating the methyl chloride present. When the concentration of methyl chloride is below 40 per cent, this method gives incorrect results, especially if considerable amounts of water vapor or methane are present.

Under suitable conditions, methyl chloride will burn in the presence of an excess of oxygen:

$$2\,CH_3Cl + 3\,O_2 = 2\,CO_2 + 2\,H_2O + 2\,HCl.$$

McKee and Burke[347] have used this method for the analysis of gas mixtures containing methyl chloride. The mixture is burned with an excess of oxygen in a combustion pipette having a layer about 1.5 cm. deep of 3 *M* potassium hydroxide, over the mercury. After measuring the decrease in volume, the solution of potassium hydroxide is removed, filtered to remove any mercurous oxide, then neutralized, and the chloride is determined by Mohr's or any other satisfactory method. From the quantity of chloride found, if no other chlorine compound is present, the amount of methyl chloride can be calculated.

If the analysis is properly performed, a difference between the oxygen consumed and the amount of chloride formed, indicates the presence of either a higher chlorinated compound or of some other combustible gas. This method in conjunction with the procedure of Allison and Meighan furnishes a means of analyzing mixtures containing other gases soluble in organic solvents. McKee and Burke have shown that by this method it is possible to analyze mixtures of methyl chloride with methyl ether, ethylene, carbon monoxide, carbon dioxide, hydrogen, methane, oxygen, and nitrogen, with the accuracy of ordinary gas analytical processes.

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[346] *Ind. Eng. Chem.*, **11**, 943 (1919).
[347] *Ind. Eng. Chem.*, **15**, 578 (1923).

SILICON TETRAFLUORIDE (SiF_4)

Properties of Silicon Tetrafluoride.—Specific gravity (air = 1), 3.60 density at 0°, 760 mm., 4.693 grams per liter; critical temperature, —1.5°; critical pressure, 50 atmospheres; melting point, —77°.

The gas is completely absorbed by water, and is at the same time decomposed:

$$3\,SiF_4 + 4\,H_2O = Si\,(OH)_4 + 2\,H_2SiF_6.$$

This reaction which has been employed by Fresenius[348] for the quantitative determination of fluorine, might possibly be made use of for the determination of silicon tetrafluoride in gases.

PHOSPHINE (PH_3)

Properties of Phosphine.—Specific gravity (air = 1), 1.175; density at 0°, 760 mm., 1.5293 grams per liter; critical temperature, 51.3°; critical pressures, 64.5 atmospheres; boiling point, —87.4°; melting point, —132.5°.

Phosphine is a colorless gas with a very unpleasant odor resembling that of decayed fish. It is very poisonous. The pure gas takes fire only at a temperature above 100°. It can be mixed with pure oxygen without change, but if the mixture be suddenly brought under diminished pressure, it explodes. Phosphine takes fire when brought in contact with a drop of fuming nitric acid, or with chlorine or bromine.

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[348] Fresenius, *Quant. chemische Analyse*, 6th ed., Part I, p. 431.

Phosphine is somewhat soluble in water. One volume of water absorbs 0.26 volume [349] of the gas at 17°, and takes on its odor and a disgusting taste. Exposed to the light, the solution decomposes with evolution of hydrogen and separation of amorphous phosphorus. The gas is decomposed by the electric spark into phosphorus and hydrogen.

When a strip of silver nitrate test paper is brought into contact with the gas, the paper is at once blackened, metallic silver and phosphoric acid being formed.

If phosphine is passed through a neutral acqueous solution of potassium mercuric iodide, a crystalline, orange-yellow precipitate, PHg_3I_3 is produced.[350]

Determination of Phosphine.—Phosphine may be determined by converting it into phosphoric acid either by burning it or by passing it through bromine water or a solution of sodium hypochlorite [351] and precipitating the resulting phosphoric acid with magnesia mixture. These reactions may also be utilized for the detection of phosphine in a gas mixture, the phosphoric acid being identified by precipitation with ammonium molybdate.

Moser and Brukl [352] have made a study of the gravimetric determination of phosphine and have described a new absorption apparatus for making this analysis.

The reaction which they utilize is

$$8\,HIO_3 + 5\,PH_3 = 5\,H_3PO_4 + 8\,I + 4\,H_2O.$$

A 2 N solution of iodic acid is employed. The iodine is distilled off in a current of carbon dioxide, and it is immaterial whether the liberated iodine is titrated or the phosphoric acid determined as magnesium pyrophosphate, although the latter method is recommended.

Phosphine may also be absorbed by an excess of a solution of silver nitrate,

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[349] Stock, Böttcher and Lenger, *Ber.*, **42**, 2855 (1909).

[350] Lemoult, *Compt. rend.*, **139**, 478 (1904).

[351] Lunge and Cedercreuz, *Z. angew. Chem.*, **10**, 651 (1897).

[352] *Z. anorg. allgem. Chem.*, **121**, 73, 313 (1922).

$$8\,AgNO_3 + PH_3 + 4\,H_2O = H_3PO_4 + 8\,Ag + 8\,HNO_3.$$

Because of the probability of slight explosions during the absorption, a special apparatus was devised. The silver was dissolved in nitric acid, precipitated with hydrochloric acid, and the phosphoric acid was determined in the filtrate as magnesium pyrophosphate. With concentrated silver nitrate, a colloid of the composition $Ag_3P \cdot 3\,AgNO_3$ is formed. With ammoniacal silver nitrate the results from the weight of silver deposited are always low.

Phosphine may also be absorbed by a solution of mercuric chloride:

$$6\,HgCl_2 + PH_3 + 3\,H_2O = H_3PO_3 + 6\,HCl + 6\,HgCl$$
$$8\,HgCl_2 + PH_3 + 4\,H_2O = H_3PO_4 + 8\,HCl + 8\,HgCl.$$

After complete absorption and oxidation with nitric acid, the phosphoric acid can be precipitated as magnesium ammonium phosphate.

With auric chloride the reaction for the absorption is:

$$8\,AuCl_3 + 3\,PH_3 + 12\,H_2O = 8\,Au + 24\,HCl + 3\,H_3PO_4.$$

The gold still in solution can be precipitated by hydrogen sulphide, and the phosphorus determined as pyrophosphate after oxidation of any lower acids of phosphorus with bromine water.

Good results may also be obtained with a 0.2 *N* solution of copper sulphate. After absorption, the solution is oxidized with bromine water, the copper is precipitated with hydrogen sulphide, and the phosphoric acid is determined in the filtrate as magnesium pyrophosphate. There is little choice between the five methods, but perhaps the use of copper sulphate as an absorbent is least desirable. Hempel[353] claims that a sulphuric acid solution of copper sulphate is the best absorbent for phosphine in acetylene.

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[353] *Z. angew. Chem.*, **11**, 53 (1898); Hempel, *Gasanalytische Methoden* (1913), p. 223.

Further details concerning the determination of phosphine, particularly in the presence of acetylene, are given on page 387.

ARSINE (AsH_3)

Properties of Arsine.—Specific gravity (air = 1), 2.695; density at 0°, 760 mm., 3.485 grams per liter; boiling point, —54.8°; melting point, —113.5°.

Arsine is a colorless gas of very unpleasant odor. It is extremely poisonous. When passed through a highly heated tube, the gas is decomposed and a glistening mirror of metallic arsenic is deposited. The gas is slightly soluble in water.

The best confining liquid for gas mixtures that may contain arsine is a freshly boiled, concentrated solution of sodium chloride. Arsine is completely and rapidly absorbed by solutions of silver nitrate.[354]

Detection of Arsine.—Arsine may be detected by allow-the gas to act upon a crystal of silver nitrate. If the amount of arsine in the gas mixture under examination is not too great, there is formed a yellow compound which is said to be $AsAg_3 \cdot 3\ AgNO_3$. If the gas contains considerable arsine, the yellow color appears only for an instant and changes to black almost immediately. If the gas mixture contains hydrogen sulphide, this is removed by passing the gases through a glass tube that contains first a plug of cotton, then a second plug of cotton that has been moistened with a solution of ammonium lead acetate, and beyond this a crystal of silver nitrate and one of lead acetate. The latter serves to show whether any hydrogen sulphide has passed the second cotton plug.

Arsine may also be detected[355] by passing the gas into a rather concentrated ammoniacal silver solution which is at once darkened by the slightest traces of the gas. The test does not serve to detect arsine in the presence of stibine, phosphine, or hydrogen sulphide, because those gases also cause a darkening of the silver solution.

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[354] Lassaigne, *J. chim. medic.*, **16**, 685 (1840); Reckleben, Lockemann, and Eckardt, *Z. anal. Chem.*, **46**, 671 (1907).

[355] Reckleben and Lockemann, *Z. angew. Chem.*, **19**, 275 (1906).

Determination of Arsine.—Arsine cannot accurately be determined by passing the gas into a solution of silver nitrate and ascertaining either the amount of silver precipitated or of arsenious acid formed.[356] It may, however, be volumetrically determined by absorbing the gas with a neutral solution of silver nitrate or with a solution of sodium hypochlorite containing three per cent of active chlorine.

Moser [357] states that arsine and stibine may be determined with his apparatus, but he gives no details.

STIBINE (SbH_3)

Properties of Stibine.—Specific gravity (air = 1), 4.360; density at 0°, 760 mm., 5.6 grams per liter; boiling point, — 17°; melting point, — 88°.

Stibine is a colorless gas of less pronounced odor than arsine. It is but slightly soluble in water.

When stibine is passed into a solution of silver nitrate a black precipitate, $SbAg_3$, is formed. If this substance is washed with water and boiled with tartaric acid, it is decomposed with the formation of silver and a soluble compound of antimony.

When stibine acts upon a crystal of silver nitrate, the black compound, $SbAg_3$, is formed.

Stibine may be determined by passing the gas into a solution of silver nitrate, collecting the silver antimonide on a filter, washing it, decomposing it with tartaric acid and determining the antimony in solution.

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[356] Reckleben and Lockemann, *loc. cit.*

[357] *Z. anorg. allgem. Chem.*, **121**, 313 (1922).

DICHLORO-ETHYLSULPHIDE

Mustard Gas

Yablick, Perrott and Furman[358] have described a very sensitive method for the determination of traces of mustard gas in air. The gas mixture is passed through a one per cent solution of selenious acid in 1:1 sulphuric acid, heated to 85°. The dichloro-ethylsulphide reduces the selenious acid, forming an orange-red suspension of selenium which may be determined by a nephelometer colorimeter. About 0.005 mg. can be detected by this method. Arsine and substituted arsines and several other toxic gases also react with the selenious acid.

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[358] *J. Amer. Chem. Soc.*, **42**, 266 (1920).

CHAPTER XV

FLUE GAS ANALYSIS

In the examination of the efficiency of the various devices in which the chemical energy of the fuel is transformed into heat energy, it is usually necessary to determine the composition and the heating value of the fuel, and to make an analysis of the gas mixture that passes from the zone of combustion into the flue. The analysis of solid and liquid fuels does not fall within the scope of the present work, but the analysis of flue gas will here be considered, and the determination of the heating value of liquid and gaseous fuel and the analysis of combustible gas mixtures will be discussed in later chapters.

When carbon is burned in air, one volume of oxygen unites with solid carbon to form one volume of carbon dioxide. If pure carbon could be completely burned with an amount of air that contains oxygen just sufficient for the conversion of the carbon to carbon dioxide, the escaping gases would contain the same amount of carbon dioxide as there is oxygen in the air, namely, about 21 per cent. The combustible matter in commercial fuels does not, however, consist entirely of pure carbon, and consequently the theoretical amount of carbon dioxide that would be formed in their complete combustion will always lie below 21 per cent. If the attempt should be made in actual practice to cut down the air supply to the amount theoretically needed for the combustion of the fuel, incomplete combustion would result. The amount of air admitted to the fuel is, in proper firing, in excess of that theoretically necessary, with the result that the percentage of carbon dioxide in the flue gas should be about twelve to fifteen per cent.[1] With careless firing or faulty construction of the furnace the proportion of carbon dioxide in the flue gas will fall below the above amount and the per cent of oxygen in the escaping gases will correspondingly rise. The greater the excess of air admitted to the furnace the larger will be the amount of heat carried off through the flue by the gases.

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[1] Winkelmann, *Z. angew. Chem.*, **27**, Aufsatz 212 (1914); Grebel, *Chaleur et industrie*, **7**, 307, 389 (1926).

If the combustion is complete, the flue gases will consist mainly of carbon dioxide, oxygen, nitrogen, and water vapor. Some judge the completeness of the combustion by determining only the carbon dioxide in the flue gases, but such results may be misleading.[2] When combustion is incomplete, the flue gas may also contain carbon monoxide and some hydrogen and hydrocarbons. If the fuel contains sulphur, some sulphur dioxide may be present in the chimney gases, and also, in some cases, small amounts of oxides of nitrogen. Usually it is necessary to determine only carbon dioxide, oxygen, and carbon monoxide, the remainder of the gas being assumed to be nitrogen. The water vapor is usually ignored, as the analyses are generally reported on the dry basis.

Sampling of Flue Gas.—If the operator wishes merely to ascertain the percentages of these three gases in the flue gases at certain intervals, the gases from the fire may be drawn by a bottle aspirator through a tube provided with a T-tube (see Fig. 8) to which a gas burette is attached. Any other aspirating device may of course be employed in place of the bottle aspirator. It is inadmissible to collect or store over water any gas mixture containing carbon dioxide if, in the determination of that gas, results of more than approximate accuracy are desired. The small bottle *C* contains a little water which serves to indicate the speed of flow. Before a sample of the flue gases is drawn off in the Hempel burette, the pinchcocks at the top are opened and the level-tube is raised until the burette and connecting tube are filled with the confining liquid. In drawing off the sample for analysis, the pinchcocks are opened and the level-tube is slowly lowered until slightly more than 100 cc. of gas has been drawn into the burette. The two pinchcocks are then closed and the rubber tube at the top of the burette is slipped off the lower end of the glass tube *A*. If only approximate results are required, water may be used as the confining liquid in the burette. For more accurate work mercury should be employed.

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[2] Rodhe, *Elec. World*, **77**, 429, 712 (1921).

If an average sample of the flue gases covering a period of several hours is desired, the sampling tube of Huntly (see p. 6) may be employed and the sample collected over mercury. Although Huntly gives no description of the method to be followed in transferring the gas from the sample tube to a Hempel gas burette, it is obvious that this may easily and accurately be done in the following manner:

Invert the tube and fasten it in a clamp. Connect a mercury level-bulb with the capillary tube *A* by a piece of rubber tubing about 40 cm. long. Turn the stopcock *H* so that *A* communicates with the side capillary tube *B*, thus driving all air out of *A*. Connect the capillary tube *F* with the capillary connecting tube of the burette by a short piece of rubber tubing in the usual manner, and turn the stopcock *K* so that *F* opens into *E*. Open the pinchcock of the burette, raise the level-tube and in this manner fill *F* with mercury. Upon now turning the stopcock *H* and *K* to such positions that *A* and *F* communicate with *C*, and lowering the level-tube of the burette, the gas sample will be drawn over into the burette without possibility of admixture with air.

Analysis of Flue Gas.—If the sample of flue gas is taken in the neighborhood of the laboratory, the analysis may rapidly and accurately be made either with a modified form of the Haldane apparatus,[3] or with the apparatus of Hempel. If the latter is used, a sample of 100 cc. is measured off in a Hempel burette in the manner described on p. 67. The three gases, carbon dioxide, oxygen and carbon monoxide, are then absorbed in the order given, the decrease of volume in cubic centimeters in each case giving directly the percentage of the constituent in the flue gas.

[3] Burrell and Siebert, *Bureau of Mines, Tech. Paper* No. 31 (1913).

Carbon dioxide is absorbed in a Hempel simple gas pipette for solid reagents that is filled with a concentrated solution of sodium or potassium hydroxide (see p. 231). The pipette is connected with the burette in the manner that has already been described in detail on p. 68 and the complete removal of the carbon dioxide is accomplished by passing the gas mixture into the pipette, allowing it to remain there for one minute and then drawing it back into the burette. If water is being used as the confining liquid in the burette, it is allowed to run down for one minute and the residual gas volume is then read off, the diminution in volume being equal to the per cent of carbon dioxide in the flue gas. For the removal of oxygen a pipette containing phosphorus (see p. 181), alkaline pyrogallol (see p. 174) or sodium hyposulphite (see p. 187) may be employed; the manipulation described under these various reagents should be carefully followed so that the complete removal of all of the oxygen in the gas mixture may be insured. In the analysis of flue gas with the older or, indeed, with some of the later modifications of the Orsat apparatus, oxygen is not entirely removed. Since this gas is absorbed by cuprous chloride which is next used for the determination of any carbon monoxide that may be present, a diminution in volume resulting from the absorption of oxygen by the cuprous chloride would naturally be ascribed to carbon monoxide in the gas mixture. This is a frequent cause of error in the analysis and in the calculations that are based upon it.

After the oxygen has been absorbed, a double gas pipette containing ammoniacal cuprous chloride (see p. 240) is connected with the burette, the residual gas is passed over into the pipette, and the absorption of carbon monoxide is effected by gently shaking the pipette backward and forward without disconnecting it during a period of three minutes.

Any sulphur dioxide that is present in the flue gas will be absorbed by potassium hydroxide in the determination of carbon dioxide. If it is desired to determine the amount of sulphur dioxide present, a fairly large sample of the gas should be drawn directly from the flue through a tube containing a wad of cotton to stop the dust, then through a gas washing bottle containing a measured volume of a standard iodine solution and finally through a gas meter for measurement (see p. 21).

The sulphur dioxide may also be determined by passing the flue gas through bromine water and precipitating the resulting sulphuric acid as barium sulphate, or by absorbing both the carbon dioxide and sulphur dioxide in sodium hydroxide and determining the latter iodometrically.[4]

If the plant that is being tested is at a considerable distance from the laboratory, it is frequently more convenient to make the analysis of flue gas on the spot than to transport the gas sample to the laboratory. In such case some suitable form of Orsat apparatus will be found convenient.

If the Orsat-Dennis apparatus is employed, the absorption pipette next to the burette is filled with a solution of potassium or sodium hydroxide, the next pipette with a solution of sodium hyposulphite or of alkaline pyrogallol, and the third pipette with an acid solution of cuprous chloride. Carbon dioxide, oxygen and carbon monoxide are then absorbed by the three reagents in the order given. The manipulation of the apparatus is described on page 79.

Automatic Flue Gas Analysis.—The character and completeness of the combustion in a furnace or other heating apparatus may, to a considerable degree, be judged by the percentage of carbon dioxide in the gases escaping through the flue. This fact has led to the invention of numerous devices for automatically and continuously determining carbon dioxide. It is impossible, within the scope of this book, to describe the many individual forms, and the discussion must here be limited to the general principles[5] involved, with references to the various instruments.

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[4] Balthaser, *Chem. Ztg.*, **47**, 225 (1923).

[5] Braun, *J. Gasbel.*, **63**, 310, 325, 344, 388 (1920), gives an excellent summary of the different types of instruments; see also Barkley and Flagg, *Bureau of Mines, Bulletin* 91 (1916); Samter, *Z. angew. Chem.*, **20**, 1851 (1907).

I. Determination of Carbon Dioxide from the Specific Gravity

The simplest forms of apparatus based upon this principle are those in which the gas mixture is weighed. They render it possible to read off the percentage of carbon dioxide at any time, but they do not record the results. The Lux gas balance [6] and the Arndt econometer [7] are instruments of this type.

Instruments similar to the Edwards gas balance (p. 53), such as the dasymeter [8] of Siegert and Dürr, have been designed for determining the per cent of carbon dioxide by measuring the buoyant effect of the flue gas upon a globe filled with air. They also are non-recording.

Another method of determining the carbon dioxide by means of the specific gravity is represented by the Krell-Schultze apparatus.[9] The flue gas and air are drawn through two vertical communicating tubes and a very sensitive manometer, connected to the bottom of the tubes, indicates the difference in pressure, which is proportional to the difference in specific gravity. The change in the manometer may be registered photographically.

The fact that the specific gravities of two gases escaping through small openings in thin plates bear nearly the same ratio to each other as the squares of their times of escape (see p. 50) has been employed for the construction of the recording apparatus of Ubbelohde and Dommer.[10] The flue gas and air are drawn through small openings at the same pressure and temperature, and the difference in volumes is recorded continuously by two gas meters through a differential mechanism.

The fact that the pressure produced by two fans of the same capacity, resistance, and speed of rotation is directly proportional to the specific gravity of the conveyed gases, is utilized in the telezometer.[11] Using air as a compression gas, the differences in pressure vary with the specific gravity, and as the carbon dioxide is the heaviest component of the flue gas, the specific gravity of the flue gas varies with its carbon dioxide content. The apparatus is recording, but it is difficult to maintain the necessary operating conditions in service.

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[6] Lux, *J. Gasbel.*, **30**, 251 (1887); **31**, 786 (1888); **33**, 99 (1890); Samter, *Z. angew. Chem.*, **20**, 1851 (1907).

[7] *Z. angew. Chem.*, **20**, 1851 (1907).

[8] Siegert, *J. Gasbel.*, **31**, 736 (1888); Samter, *Z. angew. Chem.*, **20**, 1851 (1907).

[9] *J. Gasbel.*, **42**, 212 (1899); Samter, *Z. angew. Chem.*, **20**, 1851 (1907); *Elect. Eng.*, **49**, 671 (1909).

[10] Braun, *J. Gasbel.*, **63**, 314 (1920).

Another method [12] is based on the measurement of the changes in pressure that occur when a gas is passed under a known pressure successively through a capillary and then through an orifice in a thin plate. If the suction and the diameter and the length of the capillary tube are constant, the volume of gas passing through the capillary is inversely proportional to the viscosity of the gas, and is independent of the specific gravity. The volume of gas passing through the orifice is, however, dependent upon the specific gravity. The specific gravity and the viscosity are therefore physical properties which are independent of each other.

For example, under the same pressure, carbon dioxide passes through a capillary more rapidly than air, but more slowly through an orifice. If now the gas is passed through a tube with a capillary *A* and orifice *B* (Fig. 76), there will be a measurable pressure at *C*, which is a linear function of the carbon dioxide content of the gas. If two of these tubes, one for air and the other for flue gas, are connected to a differential manometer, the apparatus will register the carbon dioxide content on a revolving drum.

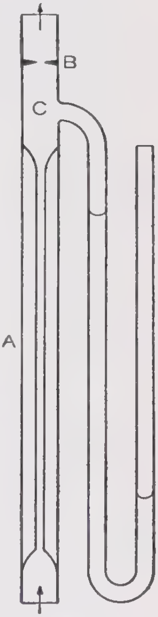

Fig. 76

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[11] Braun, *J. Gasbel.*, **63**, 314 (1920); *Bureau of Mines, Bulletin* 91 (1916), p. 23.

[12] Viehoff, *J. Gasbel.*, **63**, 155 (1920); Braun, *ibid.*, **63**, 314 (1920); Binder, *Chem. Ztg.*, **46**, 149 (1922).

Since the specific gravity of flue gas is dependent not only upon the proportion of carbon dioxide present, but also upon that of the water vapor and unburnt gases that are present, and is, moreover, variable with the pressure, the results by this method of determination cannot be as accurate as those of ordinary analysis.

II. Determination of Carbon Dioxide by Absorption

The forms of apparatus which are based on the principle of absorbing the carbon dioxide in a suitable reagent and registering the difference in volume before and after the absorptions are more reliable because they remove the specific constituent that is to be determined.

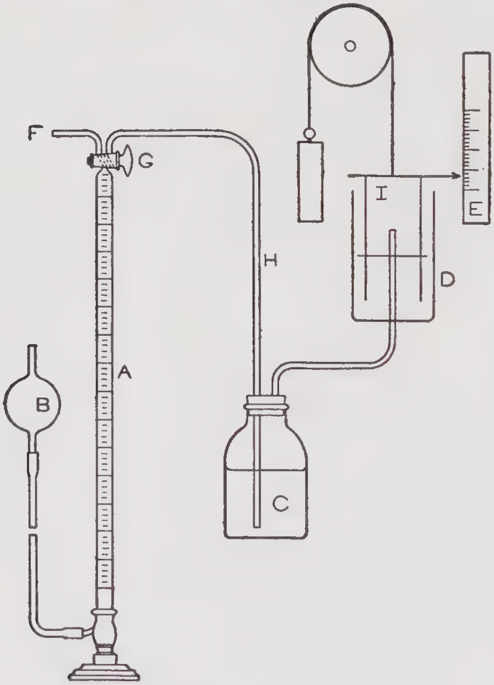

FIG. 77

The principle of operation of this type of apparatus is illustrated by Fig. 77.

A definite volume of sample of the flue gas is drawn into burette *A* through *F* by lowering the level-bulb *B*. Stopcock *G* is turned to connect with *C* through *H*. The level-bulb *B* is raised and the sample of flue gas is forced through a solution of caustic potash in *C*. The gas passing through *C* rises into the bell *I* floating in *D*, which causes *I* to rise to a height proportional to the amount of gas which enters. If no carbon dioxide is present, the entire sample will enter *I*, raising it to a height which is shown by 0 on scale *E*. The height to which *I* rises will be less the greater the amount of carbon dioxide in the gas, and scale *E* may be graduated to indicate the percentage of carbon dioxide from the position of the pointer. If the reading of the pointer and the filling and emptying of *A* and *I* are made automatic by suitable valves, the apparatus would function on the same principle as the automatic "flue gas analyzers." Examples of this type of apparatus are the Simmance-Abady,[13] Sarco,[14] and Mono[15] recorders. The latter apparatus has an auxiliary tube of copper oxide in which the carbon monoxide and combustible gases are burned to carbon dioxide, which is then absorbed. This gives an indication of the completeness of the combustion. In the Ados[16] apparatus the gas is not bubbled through the solution of caustic potash but the carbon dioxide is removed by surface absorption. The "Bi-meter CO_2 recorder"[17] measures the decrease in volume after absorption of the carbon dioxide by means of two synchronously running gas meters. The gas is passed through a water cooler prior to entering the meters to reduce the error due to variations in temperature.

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[13] Braun, *J. Gasbel.*, **63**, 329 (1920); Barkley and Flagg, *loc. cit.;* Dennis, *Gas Analysis* (1913), p. 300.

[14] Barkley and Flagg, *loc. cit.; Engineering*, **44**, 1000 (1907).

[15] Braun, *J. Gasbel.*, **63**, 345 (1920); *Met. Chem. Eng.*, **15**, 542 (1916); Harger, *Ind. Eng. Chem.*, **8**, 1035 (1916); Moeller, *Power*, **54**, 64 (1921); *Gas Age-Record*, **48**, 904 (1921); Muenzer, *Gas u. Wasserfach*, **66**, 284 (1923); Binder, *Chem. Ztg.*, **46**, 149 (1922).

[16] *Z. angew. Chem.*, **18**, 1231 (1905); Braun, *loc. cit.*

[17] *Mech. Eng.*, **28**, 572 (1911); Barkley and Flagg, *loc. cit.*

Instruments of the above type are open to the objection that the analyses are separated by intervals of several minutes, which renders it impossible to read the carbon dioxide content of the flue gas at any desired moment. This difficulty is overcome in those instruments which determine the carbon dioxide by measuring the pressure difference before and after absorption. The autolysator[18] is such an instrument; the essential parts and the principle of operation are shown in Fig. 78. *K* is a capillary tube the ends of which communicate with the differential manometer *M*. One end of *K* is connected with the regulating valve *A* which in turn is joined to a water suction-pump.

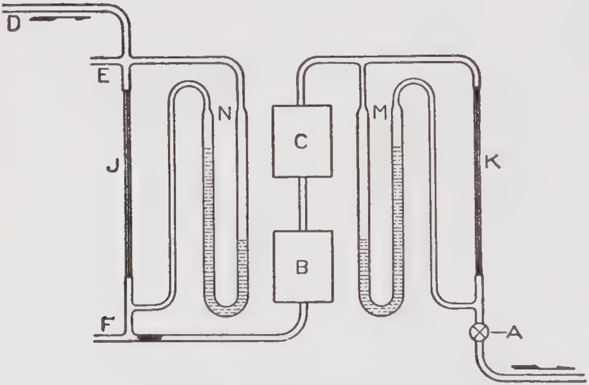

Fig. 78

The passage of the gas through the capillary *K* is dependent upon the difference in pressure shown upon the manometer *M*. If the volume of gas is kept constant by a proper adjustment of the valve *A*, the volume of gas passing through *K* is also constant. The specific gravity of the gas has no influence upon the speed of flow through the long capillary tube. The constant volume of gas passing through *K* is drawn through a second capillary *J*, the two ends of which are joined to the manometer *N*.

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[18] *Chem. Ztg.*, **30**, 1128 (1906); *Z. f. Chem. Apparatenkunde*, **2**, 57 (1907); **3**, 124 (1908); Keane, *J. Soc. Chem. Ind.*, **27**, 608 (1908); MacMullin, *Ind. Eng. Chem.*, **14**, 628 (1922).

Between the two capillary tubes are introduced the absorption vessels *B* and *C* which serve to free the gas that is passed through *J* from the constituent that is to be determined. The gas mixture under examination enters the apparatus at *D*.

It is apparent that if no gas is absorbed when the mixture passes through *B* and *C*, the same amount of gas will pass through the capillary *J* in a unit of time as flows through the capillary *K*. If the two capillaries are exactly the same diameter and length, the difference in pressure in *N* will be exactly the same as that shown by *M*. If, on the other hand, the absorption vessels *B* and *C* remove a constituent of the gas mixture, then a larger volume of gas must pass through the capillary *J* in a unit of time than through the capillary *K*. If, now, with the aid of the regulating valve *A* the reading of the manometer *M* and consequently the gas volume flowing through *K* be kept constant, the amount of gas that will pass through *J* will increase in proportion to the percentage of absorbable constituents that it contains. This will increase the difference in level of the liquid in the two arms of the manometer *N* and this difference shows directly the percentage of the absorbed constituent in the gas mixture. By means of an empirical scale attached to *N* the percentage in the gas mixture of the gas that is being absorbed in *B* and *C* may be read off at any moment. The apparatus is further provided with an automatic registering device which gives a continuous record of the percentage of absorbed gas.

Another instrument of this type is the Uehling "CO_2 Recorder,"[19] the action of which is based on the law governing the flow of gas through two apertures. This is illustrated in Fig. 79.

The flue gas is filtered before entering the chamber *N* to keep the apertures perfectly clean. *N* must be gas-tight so that no gas can enter except through *A*. When the aspirator *R* is started, the pressure in *M* will be lowered, and the gas will then flow from *N* through aperture *B* into *M*, thus reducing the pressure in *N* which will cause gas to enter through aperture *A* and establish a continuous flow of gas through both orifices. If a constant pressure of 48 inches of water is maintained in *M* and the two apertures *A* and *B* are of the same size and are kept at the same temperature, the manometer *J* will show about one-half of the pressure maintained in the first chamber, due to the fact that the apertures oppose equal resistance to the passage of the gas. This relation will be maintained so long as the same volume of gas flows through *B* as enters at *A*. If, however, a constituent of the gas, such as carbon dioxide, is continuously absorbed

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[19] *Power*, **27**, 404 (1907); *Engineering*, **111**, 626 (1921); *Met. Chem. Eng.*, **9**, 681 (1911).

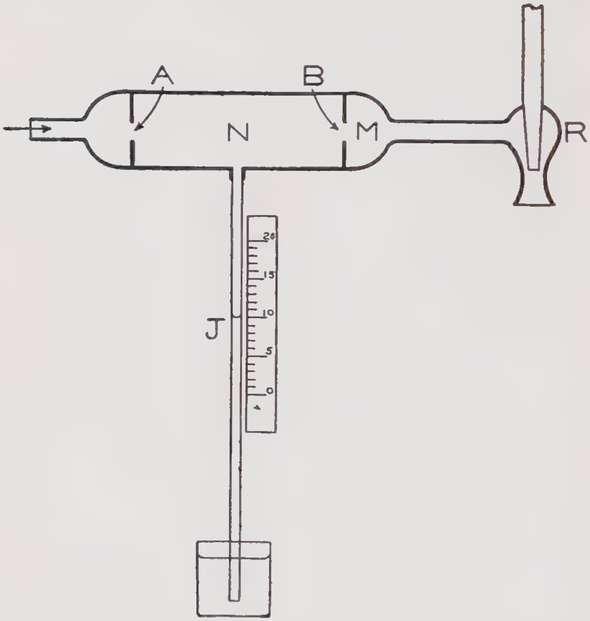

Fig. 79

when passing through *N*, the pressure therein will be correspondingly decreased. This decrease of pressure, shown by the manometer *J* or a recording gauge, therefore indicates the volume of the gas that has been absorbed. By substituting two electrically heated platinum tubes for the apertures *A* and *B*, an instrument[20] has been designed for recording carbon monoxide or other combustible constituents of flue gas.

Utilization has also been made of the heat of reaction between carbon dioxide and caustic potash in designing the "CO_2 Thermoscope"[21] for indicating the percentage of carbon dioxide in flue gas.

III. Determination of Carbon Dioxide by Thermal Conductivity

These instruments[22] are based on the fact that many gases conduct heat at different rates. (See Chap. XXI.) The principle of operation may be seen by reference to Fig. 80.

Two identical spirals of platinum wire, C_1 and C_2, are inclosed in two separate cells, the walls of which are maintained at a constant temperature. When connected to a source of constant current *B*, as one arm of a Wheatstone bridge, the temperature of the wire will rise until a point is reached where the heat supplied by the current is just balanced by the heat conducted away by the gas to the walls of the cell. The other two arms of the bridge, R_1 and R_2, are generally of manganin wire. By suitable adjustments, all loss of heat except by conduction through the gas surrounding the wire can be rendered negligible, and the temperature attained by the wire will depend upon the thermal conductivity of the gas which surrounds the wire. If the composition of the gas in one cell is different from that in the other, the thermal conductivities, and hence the cooling rates, will differ, and a difference in temperature of the two wires will result. If the wire has a high temperature coefficient of electrical resistance, a difference in temperature of the two wires will cause a deflection of the galvanometer *G*, the deflection varying directly with the difference in temperature. One cell is filled with air and sealed, and the flue gas is allowed to diffuse through the other. Since the thermal conductivity of carbon dioxide differs from that of air by approximately 40 per cent, it is possible to calibrate the reading in terms of percentages of carbon dioxide. In practice, the galvanometer is either a carbon dioxide indicator or recorder. Carbon monoxide, methane, nitrogen, and oxygen have approximately the same thermal conductivity as air, and sulphur dioxide and dust, which would interfere, are first removed by filters. The moisture content of the flue gas is kept constant by cooling it to a definite temperature before entering the cell. The accuracy is about 0.5 per cent, and the time-lag about one minute. The calibration of the instrument should be checked daily.

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[20] *Chem. Met. Eng.*, **29**, 1106 (1903).

[21] Barkley and Flagg, *loc. cit.*

[22] *Electrician*, **89**, 15 (1922); Shakespear, *ibid.*, **89**, 543 (1922); Brown Instrument Co., *Catalog* No. 32; Moeller, *Elec. World*, **79**, 293 (1922).

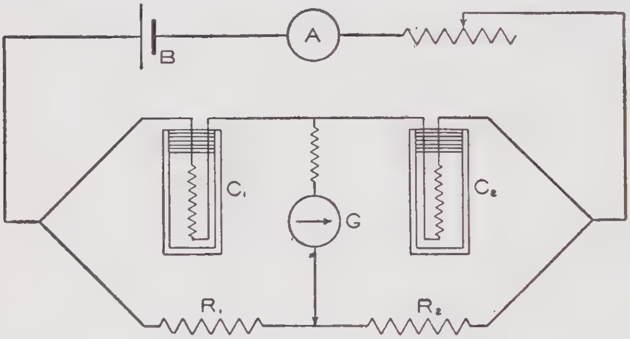

FIG. 80

IV. Determination of Carbon Dioxide by Optical Refractivity

Another type of instrument that may be used for the determination of the carbon dioxide in flue gas is the gas refractometer designed by Haber.[23] (See Chap. XXI.) This method is based on the determination of the light-refraction of the gas mixture, which may be calculated in a simple manner from the refraction of the several constituents and their partial pressures.

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[23] *Z. angew. Chem.*, **19**, 1418 (1906); *Z. Elektrochem.*, **13**, 460 (1907).

In other words, if the index of refraction, less one, is termed the refractive power, the total refractive power of a gas mixture is equal to the sum of the refractive powers of the constituent gases in the same manner as the total pressure of a gas mixture is equal to the sum of the partial pressures of the several gases that are present.

To determine the percentage of a gas in a mixture with the aid of the gas refractometer, the refraction of the mixture is first measured, and then the refraction of the residue after the removal of the constituent in question.

V. *Determination of Carbon Dioxide by Electrometric Methods*

Nordländer [24] has described a method for the determination of carbon dioxide which consists of freeing the gas from sulphur dioxide and then absorbing the carbon dioxide in a cell and measuring the change in electromotive force.

In the automatic recorder for the direct determination of carbon dioxide at low concentrations devised by Taylor and Taylor,[25] a measured volume of the gas and a measured volume of a dilute solution of ammonium hydroxide are run in together, and the change in electrolytic conductivity of the solution is determined. It may also be used for carbon monoxide by passing the gas over hot copper oxide and determining the carbon dioxide that is formed.

FLUE GAS CALCULATIONS

The amount of air used in combustion per pound of fuel, the amount of fuel gas formed, and the heat losses can be calculated from the analysis of the flue gas.

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[24] Braun, *J. Gasbel.*, **63**, 388 (1920).
[25] *Ind. Eng. Chem.*, **14**, 1008 (1922).

If pure carbon were used as fuel, air as the source of the oxygen, and all of the carbon were burned to carbon dioxide, the composition of the resulting gas should be 79 per cent nitrogen and 21 per cent carbon dioxide by volume. However, as it is always necessary to have an excess of air in order to insure complete combustion, the composition of the flue gas should be 79 per cent nitrogen and 21 per cent carbon dioxide plus oxygen. Practically none of the fuels is pure carbon; they contain varying amounts of hydrogenous material, and when this burns, water vapor is formed, which condenses when a sample is taken for analysis. This loss of water vapor causes the percentage of nitrogen in the flue gas to be greater than 79 per cent and the sum of carbon dioxide plus oxygen to be less than 21 per cent.

Because of this disappearance of some of the oxygen as condensed water, all flue gas calculations must be based upon the weight of nitrogen, which is practically unchanged in passing through the furnace and is assumed to be derived solely from the air used in combustion.

One gram molecule of any dry gas at 760 mm. and 0° has a volume of 22.4 liters. Therefore in 22.4 liters of a gas mixture, under these conditions, the weight of any component will be

$$W = \frac{\text{Molecular weight} \times \% \text{ by volume}}{100}$$

If the volume is 100 times 22.4 liters or 2240 liters, the weight of any component will be

$$W = \text{Molecular weight} \times \% \text{ by volume.}$$

Weight of Air for Combustion.—The first step is the determination of the number of pounds of entering air necessary to give 2240 liters of flue gas. This is done by first calculating the weight of nitrogen in this quantity of flue gas and then computing the weight of air equivalent to this weight of nitrogen.

$Wt. N_2 =$ Molecular weight $N_2 \times \%$ by volume in the flue gas, or

$$\text{Wt. } N_2 = 28 \times N_2.^{26}$$

Since there is 77 per cent by weight of nitrogen in air, the weight of air equivalent to this amount of nitrogen is

$$\text{Wt. air} = 28\ N_2 \times \frac{100}{77}$$

or

$$\text{Wt. air} = \frac{400\ N_2}{11} \qquad (1)$$

The weight of fuel burned is calculated from the weight of carbon in the flue gas as carbon dioxide and carbon monoxide.

$$\text{Wt. carbon} = \frac{12}{44} \times 44\ CO_2 + \frac{12}{28} \times 28\ CO,$$

or

$$\text{Wt. carbon} = 12\ (CO_2 + CO).$$

If C represents the per cent by weight of carbon in the fuel that is burned, then the weight of fuel equivalent to the carbon is,

$$\text{Wt. fuel} = 12(CO_2 + CO) \times \frac{100}{C} \qquad (2)$$

and the weight of entering air for combustion per pound of fuel is given by dividing expression (1) by (2) or

$$\frac{\text{Pounds of air}}{\text{Pounds of fuel}} = \frac{400\ N_2}{11} \times \frac{C}{1200(CO_2 + CO)},$$

or

$$\text{Pounds of air per pound of fuel} = \frac{N_2C}{33(CO_2 + CO)} \qquad (3)$$

Excess Air.—The excess of air may be determined from the ratio of the entering air to the air theoretically required. This can be computed in two ways: first, from the flue gas

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[26] In all of these calculations the per cent by volume of a constituent will be indicated by its formula.

alone; or second, from the ultimate analysis of the fuel.

The weight of air equivalent to the nitrogen in the flue gas is

$$\therefore \quad \text{Wt. air} = \frac{400\ N_2}{11} \qquad (1)$$

The weight of air equivalent to the excess oxygen minus the air necessary to oxidize the carbon monoxide to carbon dioxide, is

$$\text{Wt. air} = 100 \times 32\left(O_2 - \frac{CO}{2}\right)$$

Therefore the weight of air theoretically necessary is

$$\text{Theor. wt. air} = \frac{400\ N_2}{11} - \frac{3200}{23}\left(O_2 - \frac{CO}{2}\right)$$

$$= \frac{400}{11}\left[N_2 - 3.782\left(O_2 - \frac{CO}{2}\right)\right] \qquad (4)$$

and the ratio of the entering air to that theoretically required is given by dividing expression (1) by (4), which gives

$$\text{Ratio} = \frac{\dfrac{400\ N_2}{11}}{\dfrac{400}{11}\left[N_2 - 3.782\left(O_2 - \dfrac{CO}{2}\right)\right]},$$

or

$$\text{Ratio} = \frac{N_2}{N_2 - 3.782\left(O_2 - \dfrac{CO}{2}\right)}. \qquad (5)$$

The weight of air that is necessary to burn the fuel may be calculated from the ultimate analysis of the fuel.

$$\text{Wt. } O_2 \text{ required} = \frac{32\ C}{12} + \frac{32\ H}{4} - O$$

$$= 8\left(\frac{C}{3} + H - \frac{O}{8}\right)$$

$$\text{Wt. air required} = \frac{100}{23} \times 8\left(\frac{C}{3} + H - \frac{O}{8}\right)$$

$$= 34.78\left(\frac{C}{3} + H - \frac{O}{8}\right) \qquad (6)$$

Since from expression (3) the weight of air actually used per pound of fuel is

$$\frac{N_2C}{33(CO_2 + CO)} \qquad (3)$$

the ratio is obtained by dividing expression (3) by (6).

The ratio of the entering air to the air used may also be determined.

The weight of air not used is

$$\frac{100}{23} \times 32\ O_2,$$

and since we know from expression (1) the weight of entering air, then the

$$\text{Air used} = \frac{400\ N_2}{11} - \frac{3200}{23}O_2,$$

or

$$= \frac{400}{11}(N_2 - 3.782\ O_2),$$

and the ratio of the entering air to the air used is

$$\frac{\frac{400}{11}N_2}{\frac{400}{11}(N_2 - 3.782\ O_2)},$$

or

$$\text{Ratio} = \frac{N_2}{N_2 - 3.782\ O_2}. \qquad (7)$$

Weight of Flue Gas.—The weight of dry flue gas may be calculated from the sum of the weights of each constituent:

$$\text{Wt. gas} = 28\ N_2 + 32\ O_2 + 44\ CO_2 + 28\ CO.$$

The weight of fuel which furnishes this weight of gas was found in expression (2) to be

$$\text{Wt. fuel} = \frac{1200(CO_2 + CO)}{C} \tag{2}$$

The weight of dry gas per pound of fuel is then

$$\frac{(28\ N_2 + 32\ O_2 + 44\ CO_2 + 28\ CO)C}{1200(CO_2 + CO)},$$

or

$$\frac{C(7\ N_2 + 8\ O_2 + 11\ CO_2 + 7\ CO)}{300(CO_2 + CO)}.$$

Since $CO + N_2 = 100 - CO_2 - O_2$, the expression may be simplified to give the weight of dry gas per pound of fuel as

$$\frac{C(700 + O_2 + 4\ CO_2)}{300(CO_2 + CO)}. \tag{8}$$

The total weight of flue gas per pound of fuel, exclusive only of the moisture in the air, may be determined from the sum of the weight of the entering air and the weight of the fuel burned.

The weight of the fuel burned is

$$1 - \frac{A}{100}$$

where A is the per cent of ash as found by analysis; the weight of entering air per pound of fuel was given in expression (3).

Hence

$$\text{Wt. wet gas} = \frac{N_2C}{33(CO_2 + CO)} + 1 - \frac{A}{100}. \tag{9}$$

Heat Loss in Flue Gas.—The true heating value of coal may be determined accurately with a bomb calorimeter, but in the combustion of fuel in a furnace, the escaping gases are not cooled to the original temperature, and the water that is formed is not condensed to liquid but escapes as water vapor.

The loss of heat in the combustion of a fuel is made up of the heat carried by the flue gases, comprising:

1. Sensible heat of the dry flue gas,
2. Heat required to evaporate and superheat the water resulting from
    - (a) Free moisture of the fuel,
    - (b) Oxidation of hydrogen compounds,
3. Superheating the moisture of the air, and the loss due to
4. Incomplete combustion of carbon,
5. Unconsumed carbon in the ash.

The sensible heat carried away by the gases may be determined by multiplying their weight by the rise in temperature and by their specific heats,

Heat loss = Wt. gas × sp. heat × temperature rise.

The specific heats of gases per given weight are constant, but it was shown by Mallard and LeChatelier[27] that the specific heats of gases by volume are not constant but increase with rising temperature.

TABLE XV

Specific Heats at Constant Pressure

Range 60°–600° F.

Gas	B.t.u. per Pound
CO_2	0.222
O_2	0.217
N_2	0.241
CO	0.245

Usually, 0.24 B.t.u. per pound is taken as the specific heat of flue gas, and the sensible heat loss is

$$\text{B.t.u. per lb. of fuel} = \frac{C(700 + O_2 + 4CO_2)}{300(CO_2 + CO)} \times 0.24 \times (T - t) \quad (10)$$

in which T = temperature of flue gas 0° F.,
and t = temperature of entering air 0° F.

The loss of heat from the water of the fuel may be calculated as follows:

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[27] *Ann. der Physik.*, **23**, 809 (1907).

$$\text{Wt. free moisture per pound of fuel} = \frac{\%H_2O}{100}$$

$$\text{Wt. of water formed per pound of fuel} = \frac{\%H}{100} \times 9,$$

since 1 pound of H unites with 8 pounds of O to form 9 pounds of steam.

$$\text{Total weight of water} = \frac{H_2O + 9\ H}{100}.$$

Since the specific heat of liquid water is 1, and the specific heat of water vapor is 0.467 B.t.u. per pound, and the heat of evaporation of water is 970.4 B.t.u. per pound, the loss of heat will be

$$\frac{H_2O + 9H}{100} \times \left((212 - t) + 970.4 + 0.467(T - 212)\right) \quad (11)$$

The loss of heat due to superheating the moisture in the entering air from atmospheric temperature, t, to the temperature of the flue gases, T, per pound of fuel is

$$\text{Heat loss} = H_2O \times 0.467(T - t) \quad (12)$$

where H_2O is the weight of moisture in air per pound of fuel. This may be calculated from the formula,

$$\text{Wt. } H_2O = \text{Wt. air per pound of fuel} \times \text{wt. } H_2O \text{ per pound of air.}$$

The volume of water per volume of air is

$$\frac{\text{Relative humidity}}{100} \times \frac{\text{aqueous tension}}{\text{barometric pressure}}.$$

Therefore the weight of water per pound of air is

$$\frac{\text{Relative humidity}}{100} \times \frac{\text{aqueous tension}}{\text{barometric pressure}} \times \frac{\text{density water vapor}}{\text{density of air}}.$$

Hence it follows that

$$\text{Wt. moisture per pound of fuel} = \frac{N_2C}{33(CO_2 + CO)}$$

$$\times \frac{\text{relative humidity}}{100} \times \frac{\text{aqueous tension}}{\text{barometric pressure}} \times 0.621.$$

The loss of heat due to incomplete combustion of the carbon of the fuel in B.t.u. per pound of fuel is

$$\text{Loss} = \frac{10{,}150\,\text{C} \times \text{CO}}{100(\text{CO}_2 + \text{CO})}$$

where 10,150 is the difference between 14,550 and 4,400, or the heat evolved in burning one pound of carbon to carbon dioxide and to carbon monoxide.

$$\frac{\text{CO}}{\text{CO}_2 + \text{CO}}$$

is the fraction of carbon burned to carbon monoxide, and

$$\frac{\text{C}}{100} \times \frac{\text{CO}}{(\text{CO}_2 + \text{CO})}$$

is the weight of carbon burned to carbon monoxide per pound of fuel, in which C is the per cent carbon in the fuel actually burned. This equals the per cent of carbon in the fuel less the per cent of unconsumed carbon in the ash.

The loss of heat due to incomplete combustion is therefore

$$\text{Loss} = \frac{101.5\,\text{C} \times \text{CO}}{\text{CO}_2 + \text{CO}} \tag{13}$$

The loss due to the unconsumed carbon in the ash is

$$\text{Loss} = \frac{\text{KA} \times 14{,}550}{10{,}000}$$

where K = per cent of carbon in the ash, and A = per cent of ash as found in an actual boiler test. This is not the value found by an analysis, but should properly include the unconsumed particles carried up the stack and into the boiler setting. $\frac{\text{KA}}{10000}$ is the weight of carbon in the ash per pound of fuel. This heat loss per pound of fuel is therefore

$$\text{Loss} = 1.455\ \text{KA} \tag{14}$$

The total accountable loss of heat per pound of fuel is therefore the sum of expressions (10), (11), (12), (13), and (14).

CHAPTER XVI

ILLUMINATING GAS—FUEL GAS

COAL GAS—NATURAL GAS

The gas mixtures that fall under the above heading show great differences in composition, but they are here grouped together because the methods employed for their analysis and the sequence of the several determinations are closely similar and, in many cases, identical.

One of the most complex of these gas mixtures is that which results from the destructive distillation of coal, a product termed *coal gas.* A detailed description of the methods employed in the examination of this gas is given in the following pages, and will be found to include practically all of the points involved in the analysis of the other gas mixtures enumerated at the head of this chapter.

COAL GAS

Although the quantitative composition of coal gas varies with the methods employed in its manufacture and with the nature of the coal, the constituents of the product are nearly the same in every case. The washed gas contains carbon dioxide, carbon monoxide, hydrogen, methane, heavy hydrocarbons (illuminants), vapors of other hydrocarbons such as benzene and naphthalene, gaseous compounds of sulphur, water vapor, nitrogen, oxygen, and sometimes cyanogen or hydrogen cyanide. The unwashed gas contains ammonia and uncondensed tar, in addition to the above ingredients.

The complete examination of coal gas comprises:

1. The determination of the illuminating power of the gas;
2. The determination of the specific gravity of the gas;

3. The gas volumetric determination of the principal constituents of the gas mixture;
4. The determination of naphthalene;
5. The determination of the total sulphur in the gas;
6. The determination of the total cyanogen in the gas;
7. The determination of the heating value of the gas (see Chapter XVII).

1. The Determination of the Illuminating Power of Coal Gas

"Gas was originally used almost exclusively for open-flame lighting and naturally, therefore, most of the early requirements as to the quality of the gas related to the amount of light produced in such burners, *i.e.*, to the open-flame candle power of the gas. However, at the present time, cooking, water heating, mantle lighting, and industrial applications of gas consume by far the larger percentage of the total gas made, and in these operations it is the heat given out in combustion of the gas that is of importance to the user. Only a few per cent of the gas distributed in this country is used in open flames, and in fact, probably not over 2 per cent of it should be so used, considering only economy to the consumer.

"As a result of this change in conditions, heating value requirements have largely displaced candle power requirements. In fact, the situation has so changed that there is no longer any justification for the adoption of new candle power regulations. In the future it is to be expected that candle power measurements will be utilized, not as a test of the quality of the gas, but rather as a test of the performance of gas mantles and gas-lighting appliances and installations in which the heating value of the gas is really the important factor."[1]

In the measurement of the intensity of sources of light, two general methods are employed, the direct-comparison method and the substitution method. In the first, the light whose intensity is to be measured is placed on one side of the photometric apparatus and the standard light on the other side and the two are directly compared. In the second, a light of convenient intensity is compared with the standard; the standard is then removed and the light whose intensity is to be compared is then put in its place. The intensity of the last light in the terms of the standard is then computed.

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[1] *U. S. Bureau of Standards, Circular* No. 32 (1920), p. 24; Rosa and McBride, *J. Frank. Inst.*, **175**, 163 (1913).

While the substitution method is in general superior to that of direct comparison, the latter is usually employed in the industrial measurement of the illuminating power of gases.

For further details concerning this determination the reader is referred to special publications upon the subject.[2]

2. The Determination of the Specific Gravity of Coal Gas

The specific gravity of coal gas is usually determined by measuring its time of escape through a small opening. Methods that may be employed for this purpose are described in Chapter IV.

3. The Gas-Volumetric Analysis of Coal Gas

The volumetric analysis of coal gas comprises the determination of such constituents as are present in amounts sufficient to permit of their accurate determination in a sample of not more than 100 cubic centimeters.

These gases usually are:

1. Carbon dioxide,
2. Benzene,
3. Other heavy hydrocarbons, chiefly ethylene,
4. Oxygen,
5. Carbon monoxide,
6. Hydrogen,
7. Methane (and sometimes ethane),
8. Nitrogen.

[2] Liebenthal, *Praktische Photometrie* (1907); Rosa, *Photometric Units and Standards, Lectures on Illuminating Engineering* (1911); White, *Gas and Fuel Analysis* (1920); Jones, *Am. Gas Light J.*, **101**, 251 (1914); Rosa, Crittenden and Taylor, *Trans. Illum. Eng. Soc.*, **10**, 843 (1915); *J. Gas. Lighting*, **132**, 27 (1915); Pierce, *Am. Gas. Light J.*, **105**, 97 (1916).

Inasmuch as methods for the determination of these various gases have already been described in Chapter XIV, there will here be given only a description of the successive steps employed in a complete volumetric analysis of coal gas, together with such details of the manipulation as have not previously been discussed.

The Determination of the Absorbable Gases. Apparatus.—In the opinion of the authors, the best form of apparatus for the rapid and *accurate* determination of the absorbable constituents of coal gas, numbers 1 to 5 inclusive in the above list, is that of Hempel. The Orsat-Dennis apparatus gives equally good results, but if constructed with the six absorption pipettes that are needed for the removal of the five absorbable gases, it becomes so unwieldy that it cannot be recommended for this purpose.

For usual technical practice, a Hempel gas burette without water jacket may be employed, although somewhat more accurate results can be obtained with the use of a water mantle around the burette. If the room in which the analysis is carried on undergoes fluctuations of temperature, a water-jacketed burette should be used in all cases. The accuracy of the analysis is of course increased by the use of mercury as the confining liquid in the burette, but the differences between the results obtained over mercury and over water are usually not great enough to warrant the employment of mercury in technical practice.

The sample of gas to be analyzed is measured in a burette (see p. 67) and the absorbable constituents are determined by connecting the burette to a pipette (see Fig. 36) containing the proper reagent, and removing the different constituents by absorption (see p. 68 *et seq.*) in the following order.

CARBON DIOXIDE.—The carbon dioxide is removed by a solution of caustic potash or caustic soda (see p. 231).

For the determination of carbon dioxide in unpurified coal gas, the apparatus of Rüdorff[3] is sometimes employed. It consists of a large flask or bottle of known capacity (about one liter) which has three openings at the top, into one of which is inserted an exit tube and an inlet tube for introducing the gas, the other two containing a burette and a manometer respectively. The gas is collected in the bottle under atmospheric pressure. The carbon dioxide is absorbed by running in a solution of caustic soda from the burette until the decrease in volume caused by the absorption of the carbon dioxide is replaced by the solution as shown by the manometer. Then the amount of liquid run out of the burette indicates the volume of carbon dioxide absorbed. Göckel[4] has modified the apparatus so that there is only one ground neck to the flask.

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[3] *J. Gasbel.*, **8**, 258 (1865).

BENZENE.—Benzene is rapidly absorbed by fuming sulphuric acid and this reagent may be employed for the determination of the gas if no other heavy hydrocarbons are present. This, however, is rarely the case, and the importance of benzene as an illuminant renders very desirable the perfection of a method for the accurate volumetric separation and determination of benzene vapor in the presence of other of the heavy hydrocarbons.

Absorption of Benzene by Alcohol.—In 1891 Hempel and Dennis[5] proposed a method for the removal of the benzene vapor that was based on the ready absorption of that substance by absolute alcohol. They used a mercury pipette (Fig. 49) that contained above the mercury 1 cc. of absolute alcohol that was first saturated with the illuminating gas under examination. After the removal of the benzene the residual alcohol vapor was absorbed by passing the gas residue into a mercury pipette containing 1 cc. of water.

Further examination of this method by Dennis and O'Neill[6] demonstrated, however that the removal of benzene vapor by alcohol is not complete and that furthermore the solubility of various gases in alcohol[7] is so appreciable that errors arising from this cause cannot be entirely eliminated by saturation of the alcohol with these gases.

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[4] *J. Gasbel.*, **55**, 823 (1912).

[5] *Ber.*, **24**, 1162 (1891).

[6] *J. Am. Chem. Soc.*, **25**, 503 (1903).

[7] Lunge, *Chemisch-technische Untersuchungsmethoden*, **2**, 585.

Absorption of Benzene with Nickel Solution.—Dennis and O'Neill[8] developed a gas volumetric method for the determination of benzene which is based upon the use of an ammoniacal solution of nickel nitrate. The results obtained with this method by different analysts were, however, quite discordant. Some chemists[9] found the method to be very accurate while others reported it to be far from satisfactory. A careful examination of the statements from different analysts rendered it probable that those samples of illuminating gas with which the method gave good results contain the cyanogen compounds necessary to the formation of the compound, $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$, described by Hofmann and Küspert,[10] and that the poor results on other samples of illuminating gas might be due to the absence of cyanogen compounds in the gas. Consequently the solution of ammonia nickel nitrate was replaced[11] by a solution of ammonia nickel cyanide. This reagent was found to absorb benzene rapidly and quantitatively from mixtures of benzene vapor with air as well as from samples of illuminating gas, and it was further demonstrated that ethylene was not taken up by the solution. The reagent is prepared as follows:

To 50 grams of nickel sulphate ($NiSO_4 \cdot 7\ H_2O$), dissolved in 75 cc. of water, is added 25 grams of potassium cyanide dissolved in 40 cc. of water. After the addition of 125 cc. of ammonium hydroxide (sp. gr. 0.9) the mixture is shaken until the nickel cyanide has completely dissolved. It is then cooled to 0° C. and allowed to stand at that temperature for twenty minutes. The clear liquid is decanted from the crystals of potassium sulphate that have separated, and is treated with a solution prepared by dissolving 18 grams of crystallized citric acid in 10 cc. of water. After the mixture has stood again at 0° for ten minutes, the greenish blue supernatant solution is decanted and is introduced into a gas pipette. Two drops of liquid benzene are now added to the reagent and the pipette is shaken until the benzene has combined with the reagent, which is evidenced by the appearance of a fine, granular, white precipitate in the pipette. This is effected in two or three minutes. This addition of benzene to the reagent is made because it has been found that a freshly prepared solution of the ammonia nickel cyanide does not actively remove benzene vapor until some of the compound between benzene and the reagent has been formed.

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[8] *Loc. cit.*

[9] Pfeiffer, *Z. angew. Chem.*, **20**, 22 (1907); Stavorinus, *Het. Gas*, 554 (1906); *J. Gasbel.*, **49**, 272 (1906).

[10] *Z. anorg. Chem.*, **15**, 204 (1897).

[11] Dennis and McCarthy, *J. Am. Chem. Soc.*, **30**, 233 (1908).

The reagent is placed in a Hempel double gas pipette for solid reagents (Fig. 40), the large bulb of the pipette being filled with broken glass. The absorbent is brought into the first two bulbs, and water is introduced into the third and fourth bulbs. 100 cc. of the reagent in the pipette may be used in analytical work for the absorption of 500 cc. of benzene vapor.

In determining benzene by this method the gas mixture is repeatedly passed over into the pipette and drawn back into the burette during a period of about three minutes, which will suffice for the removal of the benzene in amounts up to about eight per cent. The gas is finally drawn into the burette which is then joined to a double pipette of the form shown in Fig. 40. The bulb *A* is filled with glass tubes and *A* and *B* are then charged with a five per cent solution of sulphuric acid. Bulbs *C* and *D* are filled with sufficient water to protect the reagent from the air. The gas residue is now passed back and forth about two minutes to remove the ammonia that enters the gas mixture from the reagent. If mercury is used as the confining liquid in the burette, the small amount of water that usually covers its surface will absorb ammonia from the reagent. This may rapidly be removed by drawing into the burette from the pipette sufficient dilute sulphuric acid to completely neutralize the ammonium hydroxide thus formed and then driving the acid back into the burette.

The reagent, must of course first be shaken with samples of the gas mixture under analysis in order to saturate the absorbents with those constituents of the mixture which they do not absorb.

This method in technical practice has been found to give uniform and accurate results.[12] It is true that Harding and Taylor[13] reported that the method is not satisfactory, but they compared the results with those obtained by another method of dubious accuracy.[14] But a careful study[15] of the procedure by Mr. Davies in the Cornell laboratory demonstrated that the solutions of ammoniacal nickel cyanide and 5 per cent sulphuric acid do not gradually absorb constituents of the gas mixture other than benzene.

That acetylene dissolves both in the reagent and in the five per cent sulphuric acid is not at all surprising because that gas is quite soluble even in distilled water. The point is quite beside the question in the present case because acetylene does not occur as a constituent of ordinary illuminating gas.

Condensation of Benzene.—Another suitable method for the determination of benzene and its homologues in coal gas is that proposed by Sainte-Claire-Deville.[16] They are determined by passing the gas, dried by calcium chloride, through a cooling coil, cooled to — 22° by immersion in an ice-salt mixture, where the condensed hydrocarbons are collected and the residual gas volume is measured by means of an ordinary meter. Berl, Andress, and Müller[17] did not find this method satisfactory for small amounts of benzene because the benzene was not entirely removed. However, Sainte-Claire-Deville recommends[18] that when the gas contains only a little benzene, the condenser be cooled to about — 72° by immersion in a paste of acetone and solid carbon dioxide in a Dewar flask. After condensation, the tube is removed from the flask and allowed to assume the temperature of the laboratory. The excess of gas escapes, and the volume of condensate is measured and finally weighed. The weight of benzene per unit volume may then be calculated by allowing for the volume of vapor condensed. Burrell and Robertson[19] have devised a modification of this method in which the gas, freed from carbon dioxide and water vapor, is cooled to — 78°, and the gases other than benzene are removed with a mercury pump. The cooling medium is then removed, the condensed liquid is allowed to vaporize, and the pressure is measured by a manometer. From this pressure and the original pressure of the gas, the percentage of benzene may be calculated. Whiton,[20] however, claims that this method is suitable only for comparative values and not absolute results.

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[12] McCarthy, *J. Gasbel.*, **55**, 891 (1912).

[13] *Ind. Eng. Chem.*, **2**, 345 (1910).

[14] Haber, *J. Gasbel.*, **43**, 511 (1900).

[15] Dennis, *Gas Analysis* (1913), p. 259.

[16] *J. Gasbel.*, **32**, 652 (1889).

[17] *Z. angew. Chem.*, **34**, 125 (1921).

[18] *Gas World*, **70**, 18 (1919); *Gas. J.*, **145**, 272 (1919), **147**, 392 (1919); Newbeck, *J. Gasbel.*, **58**, 616 (1915).

Absorption of Benzene by Paraffin Oil.—The removal of benzene by cooled paraffin oil was proposed by Müller.[21] The gas mixture is first dried by passing it through apparatus containing calcium chloride and is then slowly passed through an absorption apparatus containing liquid paraffin of 0.88 to 0.89 specific gravity and of a boiling-point of about 360°. The absorption apparatus is weighed before the experiment, is cooled during the experiment with a freezing mixture of ice and salt, and after the absorption is brought to room temperature and again weighed. The amount of gas that is passed through the absorbent is measured by a gas meter placed after the absorption apparatus. This method has been recommended by Krieger[22] and others,[23] but Berl, Andress, and Müller[24] claim that it is unsatisfactory.

[19] *Ind. Eng. Chem.*, **7**, 669 (1915); *Bureau of Mines, Tech. Paper* No. 104 (1915), p. 26.

[20] *Ind. Eng. Chem.*, **8**, 733 (1916).

[21] *J. Gasbel.*, **41**, 433 (1898).

[22] *J. Gasbel.*, **58**, 61 (1915); *Z. angew. Chem.*, **34**, 192 (1921); *Chem. Ztg.*, **46**, 468 (1922).

[23] Neubeck, *J. Gasbel.*, **58**, 616 (1915); Rothkopf, *Gas World*, **66**, 406 (1917); Copp, *ibid.*, **66**, 222 (1917); Shuttleworth, *Gas World*, **72**, 15 (1920); Than, *Chem. Age* (London), **7**, 636 (1922).

[24] *Z. angew. Chem.*, **34**, 125, 278 (1921).

Determination of Benzene as Dinitrobenzene.—Harbeck and Lunge[25] devised a method for the determination of benzene that is based upon the fact that benzene, when present in a gas mixture in relatively small amount, is quantitatively converted into dinitrobenzene when the gases are passed through a suitable absorption apparatus containing a mixture of equal weights of concentrated sulphuric acid and fuming nitric acid. The dinitrobenzene, which is difficultly soluble in water but easily soluble in ether, is extracted with ether and, after evaporation of the solvent, is weighed. From this weight the amount of benzene in the gas is calculated. The method is quite accurate, but unfortunately it is so time-consuming as to preclude its use in routine analysis.

Pfeiffer determines[26] the dinitrobenzene obtained by the Harbeck and Lunge method by a volumetric procedure based upon the reaction first mentioned by Limpricht[27] in which the dinitrobenzene is reduced to diamidobenzene by stannous chloride and the excess of the reducing agent is determined by titration with an iodine solution of known strength. The reactions involved are

$$C_6H_4(NO_2)_2 + 6\ SnCl_2 + 12\ HCl = C_6H_4(NH_2)_2 + 6\ SnCl_4 + 4\ H_2O,$$

$$SnCl_2 + 2\ I + 2\ HCl = SnCl_4 + 2\ HI.$$

Separation of Benzene from Ethylene.—In the method of Haber and Oechelhäuser[28] the total amount of the heavy hydrocarbons is determined by means of fuming sulphuric acid, and the ethylene in another sample is determined by absorption in bromine water of known strength and titration of the residual free bromine with sodium thiosulphate. Assuming that only benzene and ethylene are present the amount of benzene is equal to the difference between these two results.

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[25] *Z. anorg. Chem.*, **16**, 41 (1898); also *Chemisch-technische Untersuchungsmethoden*, **2**, 592.

[26] *Chem. Ztg.*, **28**, 884 (1904).

[27] *Ber.*, **11**, 35 (1878).

[28] *J. Gasbel.*, **39**, 799 (1896); **43**, 347 (1900).

The method gives fairly accurate results, but it is open to the objection that, for benzene, it is indirect and that a determination takes considerable time.

Differential Pressure Method.—Davis and Davis[29] have described a differential pressure method for the determination of benzene, etc., in gases. The apparatus consists of a pair of flasks connected to a differential manometer. One flask is filled at atmospheric pressure with the gas containing the vapor to be determined. The other flask is filled at the same pressure with gas containing none of the vapor. The gas in each flask is then saturated with the vapor to be determined and the differential pressure shown is a measure of the partial pressure of the vapor originally present in the gas.

Adsorption by Charcoal.—Berl, Andress, and Müller[30] have proposed the use of active charcoal for the determination of benzene in illuminating gas. The gas is passed at the rate of 250 liters per hour through 30 to 40 grams of charcoal in a U-tube until the charcoal has gained about 25 per cent in weight. The tube is then heated to 110° to 120°, steam is passed through, and the oil is condensed and measured in a burette. If the tube is evacuated at this temperature until the charcoal is dry, it is ready for another determination. The gain in weight of the charcoal cannot be used directly as it also adsorbs non-condensable vapors. This method has been widely recommended,[31] but Krieger[32] states that it is less generally applicable than hoped for, because the best conditions have not yet been determined.

OTHER HEAVY HYDROCARBONS.—The other heavy hydrocarbons are determined with a pipette containing fuming sulphuric acid, making the connection and effecting the absorption in the manner described on page 260.

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[29] *Ind. Eng. Chem.*, **10**, 709 (1918).

[30] *Z. angew. Chem.*, **34**, 125 (1921).

[31] Berl, *Z. angew. Chem.*, **35**, 332 (1922); Haber, *Chem. Ztg.*, **47**, 62 (1923); Bähr, *ibid.*, **46**, 804 (1922); Schmolke, *Gas u. Wasserfach*, **67**, 77 (1924); Gollmer, *Z. angew. Chem.*, **37**, 773 (1924); Berl and Wachendorff, *ibid.*, **37**, 205 (1924); Bürger, *Chem. Ztg.*, **48**, 161 (1924); Fischer and Zerbe, *Z. angew. Chem.*, **37**, 483 (1924).

[32] *Chem. Ztg.*, **47**, 357 (1923).

OXYGEN.—The oxygen is determined with a pipette containing phosphorus or alkaline pyrogallol or sodium hyposulphite, in the manner described in Chapter XIV for the reagent that is employed.

CARBON MONOXIDE.—For the determination of carbon monoxide, a Hempel double pipette containing ammoniacal or acid cuprous chloride (see p. 240) is used, following the procedure given on pp. 70 and 244. Some ammonia or hydrogen chloride from the reagent will now be present in the gas mixture. When water is used as the confining liquid in the burette, these gases will be absorbed by it. But when mercury is employed as the confining liquid they should be removed before the gas is measured, the ammonia by passing the gas into a pipette containing five per cent sulphuric acid, the hydrogen chloride by passing the gas into a pipette containing potassium hydroxide.

Kropf[33] states that to effect complete absorption of carbon monoxide in the analysis of generator gas, it is necessary to use three pipettes, the first two containing an acid solution of cuprous chloride and the third an ammoniacal solution. Hoffmann,[34] however, recommends that the use of cuprous chloride be omitted altogether in the analysis of producer gas, and that the three combustible gases be determined directly by combustion with oxygen.

If hydrogen, methane, and nitrogen are to be simultaneously determined in the combustion pipette (see below), the gas residue may be passed directly into this pipette after the determination of carbon monoxide. The burette that is used in the combustion is filled with mercury, not with water.

HYDROGEN, METHANE (AND ETHANE), AND NITROGEN.—These gases may be determined separately by the successive removal of hydrogen and the paraffins, or if methane is the only hydrocarbon present they may be determined simultaneously by a single explosion or combustion. If ethane is present with methane, the amounts of the two hydrocarbons cannot be determined by combustion unless the hydrogen is first removed (see Chapter XII).

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[33] *Z. angew. Chem.*, **30**, 177 (1917).
[34] *Chem. Ztg.*, **40**, 412 (1916).

For the *simultaneous* determination of hydrogen, methane and nitrogen, and of methane, ethane and nitrogen the combustion method of Dennis and Hopkins is to be preferred to the explosion of the residue with air or oxygen because in the former procedure the possibility of incomplete combustion or of the formation of measurable amounts of oxides of nitrogen is avoided, and because further the complete oxidation of the combustible gases is independent of the composition of the gas mixture. The manipulation of the combustion pipette for the simultaneous determination of hydrogen, methane and nitrogen, and the calculation of the analytical results is described in detail on pp. 145 and 258. If both methane and ethane are present with hydrogen and nitrogen in the residue remaining after the removal of the absorbable gases, the hydrogen is first removed, and the methane and ethane are then burned in the combustion pipette, the total contraction being noted, and the volume of carbon dioxide formed being ascertained.

The percentages of methane and ethane are then calculated by means of equations (7) and (8) on p. 126.

The *successive* determination of hydrogen, methane (and ethane) and nitrogen may be accomplished in a variety of ways; the hydrogen is first removed, the hydrocarbons are then burned, and the nitrogen is calculated by difference.

Of the many methods for the removal and determination of hydrogen, the most convenient and accurate is the fractional combustion with copper oxide (see p. 157). The fractional combustion with palladium asbestos cannot be recommended for the reasons set forth on pp. 151 to 155. The Hempel method of fractional combustion with palladium black (see p. 155) removes hydrogen completely, but it is open to the objection that only a small portion of the combustible residue used, with consequent multiplication of any error that may be made in the measurements.

After hydrogen has been determined by fractional combustion with copper oxide, the tube used will still contain some of the combustible residue which must be swept over into the burette with about 30 cc. of nitrogen gas from a phosphorus pipette before the combustion of the hydrocarbons is proceeded with. It is not necessary to know the volume of nitrogen that is hereby added to the gas residue, but the total volume of the residue and the nitrogen that has been added to it must be ascertained by measurement before the combustion is made.

After the removal of the hydrogen, the determination of the hydrocarbons of the paraffin series is next made. If methane is the only hydrocarbon present, the combustion may be carried out in a combustion pipette filled with water because it is here not necessary to determine the volume of carbon dioxide that is formed in the combustion. If, however, the residue contains both methane and ethane, the gas burette and the combustion pipette should be filled with mercury because both the total contraction and the volume of carbon dioxide formed must be ascertained (see p. 126).

Vail[35] finds that, in the analysis of producer gas, the residual gas, after the removal of the absorbable constituents, is too lean to be exploded, and should be enriched with oxygen and hydrogen before being burned.

NITROGEN.—It has hitherto been customary in the analysis of coal gas to state that the amount of nitrogen in the gas is equal to the final residual gas volume after the removal of the absorbable constituents and the combustible gases. Usually, however, small amounts of air are left in the connecting capillary tube when the burette and pipettes are joined together, and these minute air volumes will cause errors that, although negligible in the separate determinations, may have a cumulative effect of considerable magnitude upon the volume of residual nitrogen. For this reason it is preferable to determine nitrogen in a separate sample of the gas.

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[35] *Ind. Eng. Chem.*, **5**, 756 (1913).

This may be done by burning a sample of the gas with an excess of oxygen in a combustion pipette (see p. 143). The products of combustion are removed by means of potassium hydroxide, the excess of oxygen by an alkaline solution of pyrogallol, and the volume of the residue, which should be pure nitrogen, is then measured. If the oxygen used contains nitrogen, a correction must be applied for the amount present in the measured volume of oxygen added.

This determination may also be made by the complete combustion of the gas mixture with copper oxide by the Jäger method (see p. 157). The sample of 100 cc. is placed in a burette, the tube containing copper oxide is heated to red heat, and the gas is passed back and forth through the tube into a pipette containing a solution of sodium hydroxide until no further contraction occurs. All of the gaseous constituents, other than nitrogen, are completely removed. The residual gas volume is brought to room temperature and measured, and a correction is applied for the oxygen content of the tube of copper oxide. This correction may be eliminated by a replacing the air in the tube of copper oxide with pure nitrogen previous to the combustion. Attention should be called to the fact that while the accuracy of this method is satisfactory, the combustion of methane is very slow. The "Metrogas" apparatus[36] which works on this same principle may also be used for this determination.

4. The Determination of Naphthalene in Coal Gas

Naphthalene is a white crystalline substance that is solid at ordinary temperatures. It is, however, quite volatile and for that reason its vapor is frequently present in carburetted gas.

For the determination of naphthalene in gas mixtures the method original with Colman and Smith,[37] and modified and improved by Gair,[38] Rutten,[39] Colman,[40] Jorissen and Rutten,[41] Albrecht and Müller,[42] and Knublauch [43] is almost exclusively employed. It is based upon the fact, first noted by Fritzche,[44] that naphthalene unites with picric acid to form a crystalline compound of the formula $C_{10}H_8 \cdot C_6H_3N_3O_7$, which is but slightly soluble in a saturated or nearly saturated solution of picric acid. After absorption of the naphthalene, the excess of free picric acid is titrated with 0.1 *N* sodium hydroxide.

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[36] Evans, *Gas World*, **55**, 814 (1911); *J. Gas Lighting*, **116**, 819 (1911).

[37] *J. Soc. Chem. Ind.*, **128**, 19 (1900).

The determination may be carried out as follows: The gas is passed through a series of four wash-bottles. The first is entirely of glass and contains a 10 per cent solution of citric acid to remove any ammonia. The second, a narrow-mouth bottle of about 250 cc. capacity, is fitted with a rubber stopper and contains 100 cc. of 0.05 *N* solution of picric acid. The third contains 50 cc. of the same solution. The fourth is left empty to catch any picric acid carried over with the gas. All connections should be of glass tubing, because naphthalene is rapidly absorbed by rubber.

The standard solution of picric acid is prepared by dissolving 35 grams of picric acid in 600 cc. of boiling water; this hot solution is poured into 1800 cc. of cold water which is then well shaken. When cold, the solution is filtered, and 50 cc. of the filtrate is titrated with 0.1 *N* sodium hydroxide, using lacmoid or sodium alizarin sulphonate [45] as indicator. The solution of picric acid is then diluted to exactly 0.05 *N*.

The gas is passed through the absorption train at a rate not exceeding 1 cu. ft. per hour until about 10 cu. ft. have passed, the volume being corrected to 60° F. and 30 in. pressure. After the passage of the gas, the contents of the third and fourth bottles are washed into the second bottle, which

[38] *J. Soc. Chem. Ind.*, **24**, 1279 (1905); **26**, 1263 (1907).

[39] *Het. Gas*, Nos. 9 and 12 (1908).

[40] *J. Soc. Chem. Ind.*, **28**, 1179 (1909); *Gas J.*, **144**, 231 (1918).

[41] *J. Gasbel.*, **53**, 269 (1910); *J. Soc. Chem. Ind.*, **28**, 1179 (1909).

[42] *J. Gasbel.*, **54**, 592 (1911).

[43] *J. Gasbel.*, **59**, 525 (1916).

[44] *J. prakt. Chem.*, **73**, 282 (1858).

[45] Von Eyndhoven, *J. Gasbel.*, **59**, 107 (1916).

is then closed with a tightly fitting rubber stopper that carries a glass stopcock. The bottle is evacuated until the naphthalene picrate rises to the surface of the liquid and the stopcock is then closed. The contents is heated by immersion in a water bath with occasional shaking until the naphthalene picrate has dissolved. It is now allowed to cool, being shaken occasionally to re-dissolve any naphthalene which may sublime into the upper part of the bottle. The whole of the naphthalene is thus converted into naphthalene picrate. When the bottle has cooled to the temperature of the room, the volume of the liquid is measured, and the precipitate is removed by filtration through a dry filter paper, the first few cubic centimeters of the filtrate being discarded. 100 cc. of the filtrate is titrated with 0.1 N sodium hydroxide. If V is the difference in the number of cubic centimeters of sodium hydroxide used in the two titrations, then

$$\text{grams of naphthalene per 100 cu. ft.} = \frac{19.75\ \text{V}}{\text{volume of gas}}.$$

5. *The Determination of Total Sulphur in Coal Gas*

Illuminating gas that is prepared by the dry distillation of coal always contains hydrogen sulphide, carbon disulphide, and more complex compounds of carbon and sulphur. Although the greater part of these products is removed in the purification of the gas before it is admitted to the mains, some of the compounds are always found in the washed gas. These sulphur compounds are objectionable because of the sulphur dioxide that results from their combustion. Inasmuch as all of them form sulphur dioxide when they are burned, the determination of the total sulphur in the gas is customarily required, and usually no attempt is made to determine the separate compounds of the element that are present. Methods for the determination of hydrogen sulphide and carbon disulphide are given in Chapter XIV.

Schumacher and Feder,[46] Somerville,[47] and Hirsch[48] have described volumetric methods for the determination of sulphur which are based on the assumption that only sulphur dioxide and no sulphur trioxide is formed in the combustion of gas in the Drehschmidt type apparatus.

Of the various types of methods have been devised for the determination of total sulphur in illuminating gas, only those methods are suitable or are commonly used for official gas testing in which the gas is burned with oxygen or air, the resulting sulphur dioxide converted to sulphuric acid, and that final product determined by gravimetric or volumetric means.[49]

The U. S. Bureau of Standards[50] states: "Of the apparatus for methods of this group only the Referees, the Hinman-Jenkins, and the new model of the Drehschmidt type recently devised in the laboratories of this Bureau are recommended. Each has its particular advantage, and it is not possible to combine all of these in any one composite apparatus, nor is one of the three superior to the other two for all purposes."

The original apparatus of Drehschmidt[51] is fragile and costly and is used in few laboratories, if at all. This has been modified by Hempel[52] and by Harding.[53] A modified form devised in the Bureau of Standards[54] is shown in Fig. 81.

Determination of Sulphur by the U. S. Bureau of Standards (Drehschmidt) Method.[55]—This form of apparatus has the advantage that it will give accurate results even in a room where the air is contaminated with sulphur.

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[46] *Z. Unters. Nahr.-Genussm.,* **10**, 649 (1905).

[47] *J. Gas Lighting,* **112**, 28 (1910).

[48] *Chem. Ztg.,* **43**, 482 (1919).

[49] Among the many articles upon this subject there may be cited the following: Brügelmann, *Z. anal. Chem.,* **15**, 175 (1876); Knublauch, *Z. anal. Chem.,* **21**, 335 (1882); Poleck, *Z. anal. Chem.,* **22**, 171 (1883); Fairley, *J. Soc. Chem. Ind.,* **5**, 283 (1886); Witzeck, *J. Gasbel.,* **26**, 21 (1903); *Bureau of Standards, Tech. Paper* No. 20 (1913).

[50] *Circular* No. 48 (1916), p. 129.

[51] *Chem. Ztg.,* **11**, 1382 (1887).

[52] Hempel, *Gasanalytische Methoden,* 3d ed. (1900), p. 255.

[53] *J. Am. Chem. Soc.,* **28**, 539 (1906).

[54] *Loc. cit.;* Weaver and Edwards, *Ind. Eng. Chem.,* **7**, 620 (1915).

[55] *Bureau of Standards, Circular* No. 48 (1916).

"The burner is a porcelain tube of 3 to 4 mm. internal diameter. The gas is ignited by an electric spark between platinum terminals which are soldered to nickel leads, in order that only a short length of platinum wire will be needed. One of the leads is placed within the burner tube, its lower end being brought out through a small side tube which is sealed to the glass tube just below the rubber stopper; the wire can be held in place and the opening closed by sealing wax. The terminal outside is wired to the porcelain burner tube. The platinum wire becomes heated by the flame and thus reduces the likelihood that the flame will be extinguished by fluctuations in gas pressure. This igniter therefore eliminates the principal difficulty both of lighting and of regulating the burner which is experienced with apparatus of this type.

"The stopper which closes the lower end of the combustion chamber also serves as a connector, the porcelain burner-tube and the glass T-piece being firmly fastened into it by means of Khotinsky cement or sealing wax. The small tip through which the gas enters just above the primary air inlet is also held in with Khotinsky cement. The tip can be easily removed for cleaning, or tips of various sizes adapted to the gas to be burned can be inserted. The air necessary for complete combustion after being purified by passage through the large soda-lime tower is supplied to the flame in two portions. The primary air is drawn in by the gas as it passes through the small tip; the secondary air enters through the two inlets at the side of the combustion chamber.

"The combustion chamber, made of Jena glass tubing, is about 360 mm. long and about 25 mm. in internal diameter. The narrow tube at the top may be used for introducing water when it is desired to rinse out the apparatus; when in operation this tube is closed with a small cork. Satisfactory drainage is provided by the sloping layer of paraffin or sealing wax covering the stopper at the bottom. When the burner is lighted, the secondary inlet air keeps the base of the apparatus cool, but the rest of the combustion chamber up to the side tube is heated so that no condensation takes place on the walls. For that reason it is usually unnecessary to rinse out the combustion chamber.

"By means of a cork connector the first of a series of wash-bottles is attached to the apparatus. Rubber tubing must not be used at this point on account of the danger of introducing sulphur from it; but the wash-bottles may be connected to each other and to the suction pump by rubber tubing, which may also be used to connect the air inlets to the soda-lime tower.

"Only one wash-bottle is shown in the illustration, but three are usually required for satisfactory operation. In order that the suction may pull the gas steadily through the wash-bottles it is necessary that the end of the inlet tube of the first bottle be perforated with a number of small holes. With a single, large opening the operation of the burner is not steady. The wash-bottles may be of any of the ordinary forms.[56] Each bottle should contain enough absorbent that the products of combustion will bubble through a depth of 1 to 1½ inches of liquid.

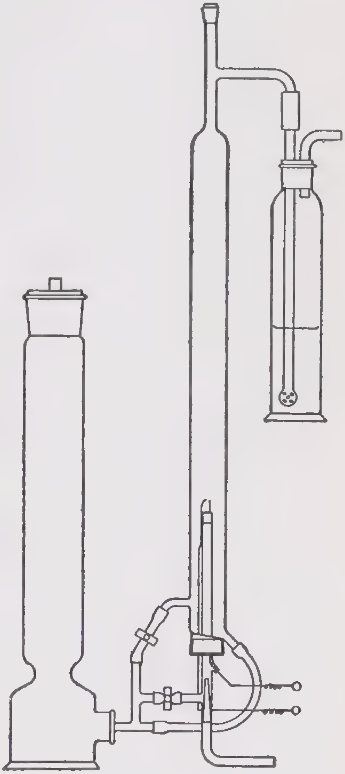

Fig. 81

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[56] See also Maze, *Chem. Met. Eng.*, **22**, 1070 (1920).

"The air is drawn in and the products of combustion are drawn through the apparatus by the suction of a small water-jet pump, or its equivalent. The spark for igniting the gas is produced by a single dry cell and an induction coil of the size rated as giving a quarter-inch spark.

"Before beginning a determination the apparatus should be adjusted to burn gas at the required rate of not more than 2.5 cubic feet per hour, and to use the proper amount of primary and secondary air. The amount of gas burned should be adjusted by removing the small glass inlet tip from the burner and reducing or enlarging the opening as required. The opening may be reduced by heating carefully in a flame; it may be enlarged by filing back the tip until the required internal diameter is reached. To adjust the air supply the wash-bottles are filled with water to the depth of 1 to 1½ inches above the lower end of inlet tubes. The jet pump is then turned on to draw air through the apparatus at a rapid rate, the battery circuit is closed to produce a continuous spark, and the gas is turned on last. This order should be followed every time the burner is lighted. If the gas is turned on before both the air flow and the spark are started, an explosion may result. As soon as the gas has ignited, the battery circuit may be opened.

"The amount of air entering the burner tube must be regulated rather carefully, so that the flame is entirely non-luminous with a clearly defined inner cone. The amount of secondary air flowing through the apparatus must, of course, be sufficient to give complete combustion. This is assured when the outer cone of the flame is steady and sharply defined. If the outline of the flame appears ragged or indistinct, some of the sulphur is certain to escape oxidation. There is little danger of having too much secondary air, but the amount is limited by the capacity of the wash-bottles. To insure complete absorption and prevent mechanical loss of the sulphate solution, it is desirable to keep this rate of air flow reasonably low, but it is better to use too much air than too little.

The primary air is regulated by the pinchcock on the inlet tube, but the adjustment of secondary air should be made by regulating the jet pump rather than by closing the air inlet.

"When these adjustments have been completed, a test for leaks should be made, the gas-supply line purged, and the meter adjusted. While the line is being purged, the soda-lime tower is filled and sufficient 5 per cent solution of potassium carbonate (K_2CO_3), with a few drops of hydrogen peroxide or of bromine water, is introduced into each wash-bottle to bring the liquid 1 to 1½ inches above the bottom of the inlet tube.

"The burner is now connected to the meter and the meter reading recorded. The suction, spark, and gas are then turned on in order, and pressure and temperature readings are made and recorded. The burner should usually be adjusted to consume about one cubic foot of gas per hour. When enough gas has been burned the gas is turned off first; then the valve controlling the jet pump is closed carefully to prevent tap-water being sucked back into the wash-bottles. The meter, barometer, thermometer, and manometer readings are again recorded. The contents of the wash-bottles are transferred to a beaker and the bottles rinsed twice with a little water. It is ordinarily unnecessary to wash out the burner chamber since it is dry at all times and the sulphur is mostly present in the form of sulphur dioxide, which passes on quantitatively. The hot walls prevent the condensation of any sulphur trioxide which may be present. The sulphate in solution is determined by one of the following methods."

GRAVIMETRIC DETERMINATION.—To the solution, which should be about 300 cc. in volume, there are added about 3 drops of a solution of methyl orange. The solution is neutralized with dilute hydrochloric acid (1:1), adding it drop by drop and then 2 cc. in excess is added. The solution is heated to boiling and 10 cc. of a hot 10 per cent solution of barium chloride is added slowly. It is then digested on a steam bath for thirty minutes and the weight of barium sulphate is determined in the usual manner.

The amount of sulphur in the gas is calculated from the weight of the barium sulphate found, the result being expressed in terms of grams of sulphur per cubic meter (1000 liters) of the gas at 0° C. and 760 mm.

Grams sulphur per cubic meter =

$$\frac{1000}{V} \times (P - P_1) \frac{\text{At. wt. sulphur}}{\text{Mol. wt. BaSO}_4} \times \frac{760(1 + 0.00367t)}{(B + b) - m}$$

In the above,

V = liters of gas burned,

P = grams $BaSO_4$ found,

P_1 = grams $BaSO_4$ found in blank test of reagents,[57]

B = observed barometric pressure,

b = pressure (in addition to atmospheric) of gas in meter,

t = temperature of gas in meter,

m = tension aqueous vapor at t°.

$$\frac{\text{At. wt. S}}{\text{Mol. wt. BaSO}_4} = 0.137325.$$

To express results as "grains sulphur per 100 cubic feet of the gas," multiply "grams per cubic meter" by the factor 43.698.

VOLUMETRIC DETERMINATION.—A number of volumetric methods have been proposed for the determination of sulphates, of which only that of Young [58] and a modification of that recommended by Hollinger [59] will be described.

In Young's method the solution containing the sulphate is treated with acetic acid in an amount sufficient to decompose the ammonium carbonate [60] that is present. The solution is then made up to definite volume and to a measured portion of it there is added a measured excess of a standard solution of barium chloride. The precipitated barium sulphate is not removed by filtration, but solution and suspended precipitate are transferred to a platinum or porcelain dish and the whole is evaporated to dryness and is then heated to low redness to expel the hydrochloric acid and ammonium chloride.[61] The dish is allowed to cool and the contents is washed out with distilled water into a beaker. An amount of a 10 per cent solution of potassium chromate sufficient to precipitate all of the barium chloride and to color the supernatant liquid pale yellow is then added, and a standard solution of silver nitrate is run in from a burette until the red color of silver chromate remains permanent. The solutions that are here used are a 0.05 *N* solution of silver nitrate that contains 8.4944 grams $AgNO_3$ to the liter and a 0.25 *N* solution of barium chloride that contains 26.0355 grams $BaCl_2$ to the liter. In the calculation of results the volume of the gas that has been burned is corrected to standard conditions (760 mm., 0° C.). The volume of barium chloride equivalent to the volume of silver nitrate that has been added (5 cc. $AgNO_3 = 1$ cc. $BaCl_2$) is then calculated, and this result is subtracted from the volume of barium chloride that was added. The remainder represents the amount of barium chloride that reacted with the sulphate in the solution. Knowing the strength of the solution of barium chloride, the actual weight of the barium chloride may then easily be calculated, and from this the grams of sulphur in the corrected volume of gas that has been burned. This final result should then be converted into the amount of sulphur in grams per cubic meter of the gas, or in grains per one hundred cubic feet of gas.

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[57] The bromine water and potassium carbonate used should be tested qualitatively for the presence of sulphates. If the test gives positive results, the sulphur is determined in a quantity of these reagents equal to that used in the experiment.

[58] Stone, *Practical Testing of Gas and Gas Meters*, p. 116.

[59] *Z. anal. Chem.*, **49**, 84 (1910); *Bureau of Standards, Circular* No. 48 (1916), p. 141.

[60] These chemicals must be free from non-volatile halogen salts.

In the modified Hollinger method 10 cc. of dilute hydrochloric acid (1:1) is added to the solution containing the sulphate, which should be about 300 cc. in volume. The solution is heated to boiling and 15 cc. of a 0.4 *N* solution of barium chloride (48.8632 g. $BaCl_2 \cdot 2H_2O$ per liter) is added. The solution is boiled for five minutes, and 15 cc. of a 0.6 *N* solution of potassium chromate (38.8404 g. K_2CrO_4 per liter) and a few drops of a 2 per cent solution of ferric chloride are added. The solution is precipitated with dilute ammonium hydroxide (1:2) and 5 cc. is added in excess. It is then boiled for five minutes, filtered and washed thoroughly with hot water. The filtrate is cooled, is then acidified with hydrochloric acid, and 2 cc. of a saturated solution of potassium iodide is added. The liberated iodine is titrated with a 0.1 *N* solution of sodium thiosulphate (24.82 g. $Na_2S_2O_3 \cdot 5H_2O$ per liter) using starch as indicator. A blank is run on 300 cc. of water in the same manner. From the amount of the solution of sodium thiosulphate that is used, less the amount required by the blank, the amount of sulphate in the solution and the grams of sulphur in the gas may be calculated.

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[61] This is present if the Referees method is used.

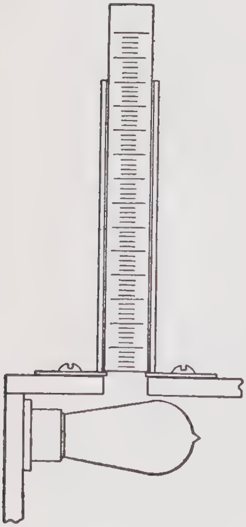

FIG. 82

TURBIDIMETRIC DETERMINATION.—The Bureau of Standards has recommended[62] this method for a rapid determination of the sulphur in the solution containing the sulphate. The solution of the sulphate is neutralized with dilute hydrochloric acid (1:1) and then 2 cc. is added in excess. The volume of the solution is measured and a 90 cc. portion taken for the test. With the solution at 25° to 30°, 10 cc. of a 10 per cent solution of barium chloride is added and the whole is vigorously stirred until precipitation is complete. The suspension is now poured, a small portion at a time, into a clean dry turbidimeter tube, graduated in centimeters (Fig. 82), until the filament of the 16 cp. carbon lamp disappears from view. This is repeated until the observed point at which the filament disappears is fixed to within one mm. The amount of sulphur present may then be determined from the curve given in Fig. 110 on page 463.

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[62] *Circular* No. 48 (1916); *Technologic Paper* No. 20 (1913); McBride and Weaver, *Ind. Eng. Chem.*, **5**, 469 (1913).

Determination of Sulphur by Referees Method.—The official method in use in England for the determination of the total sulphur in illuminating gas is known as the Referees Test and is the one most often employed in this country.

In this method the gas is burned in air that contains ammonia, and the resulting water, ammonium carbonate, ammonium sulphite, and ammonium sulphate are collected in a condensing tower. The products of combustion are then dissolved in water, the solution is acidified with hydrochloric acid, and is boiled to expel carbon dioxide. The sulphate that is present is then precipitated with a solution of barium chloride. The accuracy of the method has been called in question because of the possibility of incomplete retention of the oxides of sulphur by the condensing tower, and further because of the probability that some of the sulphur would be oxidized only to sulphur dioxide,[63] in which case the resulting ammonium sulphite would be decomposed when the solution is boiled with hydrochloric acid and some sulphur would escape precipitation as barium sulphate. These points have been investigated in the Cornell laboratory and it was found that the condensing tower that is customarily used will retain the oxides of sulphur if the rate of flow of the gas does not exceed twenty liters per hour. As to the second point, however, the analyses show that the Referees method yields too low results unless the solution of the products of combustion is treated, before acidification, with an oxidizing agent that will convert the sulphite to sulphate. With these modifications the method appears to give quite satisfactory results.

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[63] In this connection see Schumacher and Feder, *Z. Unters. Nahr.-Genussm.,* **10**, 649 (1905).

In the Referees method the gas is burned in a Bunsen burner *B* (Fig. 83), that stands in a perforated metal base *D*. The burner that is furnished with the apparatus is a small Bunsen burner with a steatite tip. With an ordinary Bunsen burner, however, the gas can be burned more rapidly, without the formation of a smoky flame, than is possible with the special burner. The products of combustion pass upward through the conical glass chimney *C*. The upper end of the chimney passes through a rubber stopper that is inserted into the tubulure of the cylinder *A*. The upper portion of the cylinder is filled with pieces of glass rod about 40 mm. long and 8 mm. in diameter, or with glass balls about 15 mm. in diameter. In the bottom of the cylinder is a round hole into which is inserted a rubber stopper that carries a glass tube. The condensed water flows through this tube into the beaker *E*.

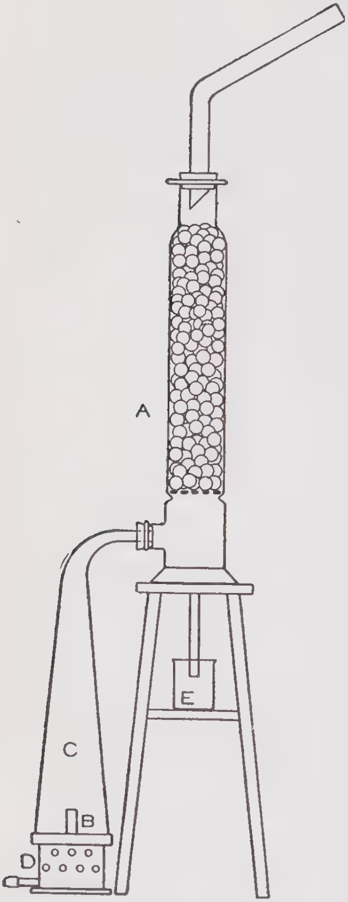

FIG. 83

Pieces of ammonium carbonate, about 40 grams in all, are placed around the burner on a perforated plate in the base *D*. A few pieces of the salt are also placed on top of the glass rods or balls in the cylinder. The ammonia that is set free by the spontaneous decomposition of this substance unites with the sulphur dioxide and prevents its escape.

The gas is first passed through a gas meter until all air has been driven from the meter and the water in the meter is saturated with the gas under examination. The meter is then connected with the burner *B* and the gas is lighted at the burner. The flame is turned down until the rate of consumption of gas is not more than 20 liters per hour. A screw clamp placed upon the rubber tube of the burner furnishes a means of accurately adjusting the height of the flame. The burner and the base *D* are then placed under the conical glass chimney and the upper end of the chimney is at once inserted into the opening of the cylinder *A*. Readings of the meter, the barometric pressure, the manometer on the meter and the temperature of the gas as it passes through the meter are immediately made.

When from 50 to 60 liters of gas has been burned, the gas is turned off and the instruments that were read at the beginning of the run are now read again. The averages of the readings of the barometer, thermometer and manometer are used in the calculation of results. The beaker *E* is replaced by a clean empty beaker and the cylinder *A* is rinsed by pouring through the tube attached to the upper opening of the cylinder two or three portions of distilled water of 25 cc. each. The chimney *C* is also rinsed out with distilled water into the beaker. These rinsings are then added to the contents of the first beaker. A measured amount, about 2 cc., of saturated bromine water is added and the liquid is thoroughly stirred for a few moments.[64] The solution is acidified with hydrochloric acid and is heated to boiling to decompose the carbonates that are present and to expel the excess of bromine.

The amount of sulphate present may then be determined either gravimetrically, volumetrically, or turbidimetrically as described in the preceding pages.

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[64] If the bromine water contains sulphates, the amount of sulphur in the volume of this reagent that is added should be subtracted from the final result. Ammonium carbonate usually contains no sulphate, but it nevertheless should be tested for this impurity before being used.

Modified forms of the Referees apparatus have been proposed by Elliott[65] and Hinman-Jenkins;[66] the form suggested by Hinman-Jenkins is shown in Fig. 84. This apparatus has the advantage of being portable; ammonium hydroxide is used in it instead of ammonium carbonate.

Methods for the determination of sulphur have also been proposed in which the compounds of sulphur are oxidized[67] or reduced[68] in the presence of a platinum catalyst or they are oxidized by alkaline perhydrol.[69]

6. *The Determination of Cyanogen in Coal Gas*

For the determination of the total cyanogen in illuminating gas the method of Nauss (p. 270) may be used.

Determination of Tar Vapors. — Clayton and Skirrow[70] and Feld[71] have described procedures for the determination of the tar fog in coal gas. The tar vapor is caught in a filter of cotton wool. The increase in weight of this filter can then be ascertained or it may be extracted with carbon disulphide and the residue weighed after evaporation of the solvent.

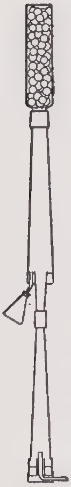

FIG. 84

NATURAL GAS

Natural gas is generally used in the unpurified state. Its composition[72] may vary greatly. Probably the most important determination is the heating value which is made with a gas calorimeter (see Chap. XVII). The sulphur may be determined as described in the preceding pages.

Many of the determinations of the constituents of natural gas have been inaccurate[73] due to the fact that some of the absorbable constituents, such as oxygen and carbon dioxide, occur in extremely small quantities. Anderson and Engelder[74] have shown that fuming sulphuric acid will absorb some gasoline vapor in addition to the illuminants, and to overcome this difficulty Brown[75] uses a one per cent solution of palladium chloride for the determination of ethylene.

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[65] *Bureau of Standards, Tech. Paper* No. 20 (1913), p. 7.

[66] Jenkins, *J. Am. Chem. Soc.*, **28**, 542 (1906).

[67] Mylius and Hüttner, *Ber.*, **49**, 1428 (1916).

[68] ter Meulen, *Rec. trav. chim.*, **41**, 112 (1922).

[69] Dickert, *J. Gasbel.*, **54**, 182 (1911); Bossard and Horst, *ibid.*, **55**, 1093 (1912); Klemmer, *Chem. Ztg.*, **46**, 79 (1922).

[70] *J. Gas Lighting*, **98**, 660 (1907).

[71] *J. Gasbel.*, **54**, 33 (1911).

[72] Burrell and Oberfell, *Bureau of Mines, Tech. Paper* No. 109 (1915); *Ind. Eng. Chem.*, **7**, 419 (1915); Mouren, *J. Chem. Soc.*, **123**, 1905 (1923); *Compt. rend.*, **178**, 1945 (1924).

Burrell and Siebert[76] have developed a method for the separation of the paraffin hydrocarbons in natural gas by fractional distillation at low temperatures (see Chap. XXI).

Anderson[77] has shown that it is difficult to burn natural gas with oxygen in a combustion pipette if a considerable amount of gasoline vapor is present. He later gave[78] detailed corrections that should be applied, but he adds that it is more logical in the case of natural gas to express the results of the combustion in the average number of carbon atoms per molecule of paraffin hydrocarbon, and the percentage of paraffin hydrocarbons in the gas. If n is the average number of carbon atoms per molecule of paraffin hydrocarbon, then

$$\mathrm{n} = \frac{3\,\mathrm{CO_2}}{2\,\mathrm{TC} - \mathrm{CO_2}}$$

V, the volume of paraffin hydrocarbon in the sample will be

$$\mathrm{V} = \frac{\mathrm{CO_2}}{\mathrm{n}}$$

and the percentage of paraffin hydrocarbon will be

$$\mathrm{P} = \frac{100\,\mathrm{V}}{\mathrm{S}} = \frac{100\,\mathrm{CO_2}}{\mathrm{Sn}}$$

where S is the volume of sample taken for combustion.

The amount of gasoline vapor in some natural gases may be high, and numerous articles have appeared from the Bureau of Mines[79] describing its determination and removal.

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[73] *Bureau of Mines, Bulletin* No. 42 (1926).

[74] *Ind. Eng. Chem.*, **6**, 989 (1914).

[75] *Met. Chem. Eng.*, **12**, 168 (1914).

[76] *J. Am. Chem. Soc.*, **36**, 1538 (1914); *Bureau of Mines, Tech. Paper* No. 104 (1915).

[77] *Ind. Eng. Chem.*, **9**, 142 (1917).

[78] Anderson, *Ind. Eng. Chem.*, **11**, 299 (1919).

[79] *Bulletins* No. 88 (1915), No. 176 (1919); *Technical Paper* No. 87 (1916), No. 253 (1920); see also Dykema and Neal, *Chem. News*, **27**, 5 (1919).

CHAPTER XVII

THE DETERMINATION OF THE HEATING VALUE OF GAS

Originally gas was used almost solely for illuminating purposes, the open, flat-flame burner being the common source of light, and the first laws and regulations related to the photometric requirements which the manufactured gas should fulfill. Later, gas was found to be useful for heating and cooking and for numerous industrial purposes in which the heating value is of greater importance than the illuminating power. At the present time probably about 95 per cent of the gas distributed is utilized solely for heating purposes,[1] the heating value being of prime importance even in the production of light with the Welsbach mantle. This has resulted in the tendency of recent legislation [2] toward the adoption of a double standard, or better of a standard heating value alone.[3]

The measurement of the heating value is known as the science of calorimetry, and the instruments employed are termed calorimeters.

The heating value or calorific power of a gas is expressed in either the metric or English system as (1) calories per liter, or (2) British thermal units (B.t.u.) per cubic foot, the latter method being the standard in this country.

The *calorie,* or small calorie, is the quantity of heat necessary to raise the temperature of one gram of water 1° C. at 15° C.

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[1] McBride, *Trans. Intern. Gas Congress* (1915); *Am. Gas Light. J.*, **104**, 99 (1916).

[2] *Bureau of Standards, Circular* No. 32 (1920).

[3] Dunn, *J. Gas Lighting,* **132**, 34 (1915); Addicks, *Met. Chem. Eng.*, **15**, 639 (1916); Phillips, *Gas Age-Record,* **48**, 620 (1921); Strache, *Z. angew. Chem.*, **36**, 601 (1924); Weaver, *Bureau of Standards, Tech. Paper* No. 290 (1915); *Gas Age-Record*, **55**, 833 (1925); Blume, *Gas u. Wasserfach,* **68**, 677 (1925); *Gas J.,* **172**, 782 (1925).

The *Calorie,* or large calorie, is the quantity of heat required to raise the temperature of one kilogram of water 1° C. at 15° C., and is equal to 1000 small calories.

On the same basis, the British thermal unit (B.t.u.) is that quantity of heat necessary to raise the temperature of one pound of water 1° Fahrenheit at 59° F.

The error introduced by the variation of the specific heat of water within the range of temperature of calorimetric experiments is so small that it usually is disregarded. The variation in the specific heat due to impurities present in the water supply is also not of sufficient magnitude to introduce any appreciable error.

For the conversion of values from one system to the other, the following factors may be used:

1 B.t.u. = 252.0 calories
Calories (small) per liter × 0.11236 = B.t.u. per cubic foot.

The heating value of a gas may be determined with a bomb calorimeter for solid fuels, but the manipulation is so difficult that the standard type of calorimeter for this purpose is one in which the gas is burned with air, and the heat produced is transferred as completely as possible to the water of the calorimeter. These instruments are of two types, namely, the continuous flow and the discontinuous flow; the former is generally employed.

Various special types of calorimeters have been devised, and it is also possible to calculate the heating value of the gas with approximate accuracy from its chemical composition and the calorific values of its constituents.

Continuous Flow Calorimeters.—In this type of calorimeter, which is generally accepted as the standard, the heating value is determined from the rise in temperature imparted to a known mass of water flowing through the calorimeter during the time that a measured amount of gas is burned.

The first instrument of this kind was that of Hartley,[4] but probably the one most widely known is that devised by Junkers[5] from which most of the calorimeters have been developed. Some of the more important improvements which have been embodied in the later instruments are placing the inlet and outlet water thermometers at the same level, radiation shields for the burner, accessibility of the parts for cleaning and repairing, and devices for diverting the effluent stream of water from the measuring vessel to the drain.

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[4] *J. Gas Lighting,* **43,** 1142 (1884).

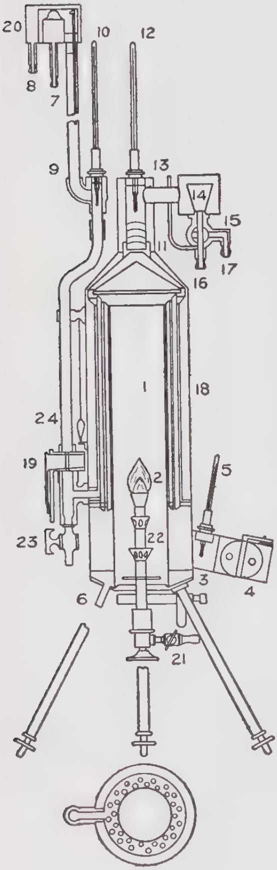

FIG. 85

The calorimeter[6] (Fig. 85) consists of an upright combustion chamber *1* through which the products of combustion from the flame *2* first rise, then pass downward through thinwalled, tinned copper tubes (shown in the cross-section), and finally escape through *3*. The rate of escape of these gases is controlled by the damper *4* and their temperature is shown by the thermometer *5* inserted through an opening in the top of pipe *3*. The water vapor in the combustion gases is partially condensed and this condensed water flows out through *6*. Cold water enters the apparatus at *7*, the excess of water overflowing to the drain through a rubber tube attached to *8*. The water passes downward through *9*, where the temperature is shown by thermometer *10* and then enters the calorimeter and passes upward through the space around the heating tubes. At the top of the calorimeter the warmed water flows through the baffle plates *11* to thoroughly mix the water before coming into contact with the bulb of the outlet thermometer *12*. It passes out of the apparatus through *13* and *14*, and then either to the measuring apparatus through *16* or to the waste through *17*, depending upon the position of the cock *15*. The water is warmed in its passage through the calorimeter, the temperature of the inlet and outlet water being measured by thermometers *10* and *12*. The calorimeter is surrounded by a polished, nickel-plated copper jacket, *18*. The rate of the flow of the water is regulated by means of the cock *19* which carries a pointer that moves along a scale, and the head is kept constant by the overflow device *20*. The rate of flow of the gas whose heating power is being determined is regulated by the cock *21*. The burner is furnished with three baffle plates, *22*, which limit eddying air currents and prevent downward radiation and consequent loss of heat. A mirror is fastened to the bottom of the instrument for observing the flame which makes it unnecessary to withdraw the burner to adjust the flame. The calorimeter should be emptied when not in use by opening cock *23*.

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[5] Bueb, *J. Gasbel.*, **36**, 81 (1893); Waidner and Mueller, *Bureau of Standards, Circular* No. 36 (1914); Strache and Glaser, *J. Gasbel.*, **58**, 742 (1915); *Met. Chem. Eng.*, **14**, 610 (1916); Pickering, *J. Soc. Chem. Ind.*, **36**, 762 (1917).

[6] Stone and Hinman, *Am. Gas Light. J.*, **101**, 387 (1914); D. McDonald and Co., *Bulletin* 403 B.

Preparation of Apparatus.—Level and adjust the wet gas meter *G* (Fig. 86) and the pressure regulator *H* and fill each with the proper amount of water (Chap. II). Connect them together with tubing, and connect the inlet tube of the gas meter with the holder or main containing the gas to be examined. All of the rubber connections should be as short as possible. Attach the burner to the outlet tube of the pressure regulator by means of rubber tubing, place the burner on the table, turn on the gas and light it at the burner. Allow the gas to burn for twenty minutes to insure the saturation of the water in the meter and pressure regulator with the constituents of the gas mixture, and the removal of air from these instruments and from the connecting tube. If the meter and regulator have been filled with fresh water, the gas should be allowed to burn about two hours. Then shut off the gas at the burner, and determine whether the hand of the meter shows any change in position to be sure that there are no leaks. In the meantime, place the calorimeter in the position shown in the figure, and level it by means of the screws at the lower ends of the legs and the plumb-bob *24*. The apparatus should be protected from drafts and the room temperature should be as nearly constant as possible. To facilitate the operation it is desirable to install the calorimeter in a cabinet[7] similar to the one shown in Fig. 87.

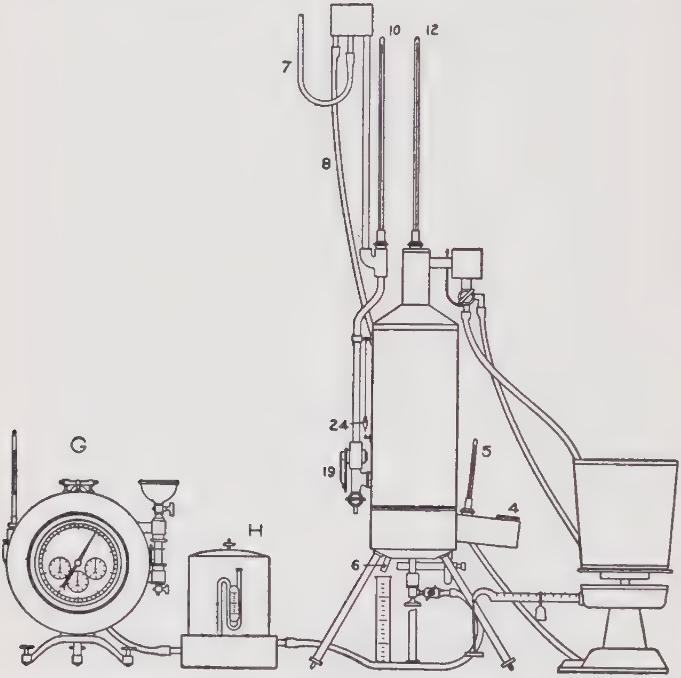

FIG. 86

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[7] *Proc. Am. Gas Inst.,* **4,** 205 (1909).

Put the thermometers *5*, *10*, and *12* (Fig. 86), in place so that the bulbs of *10* and *12* are completely surrounded by water with no dead space, and are not in contact with the metal of the calorimeter, and connect *7* with the supply of water of constant temperature by means of rubber tubing.

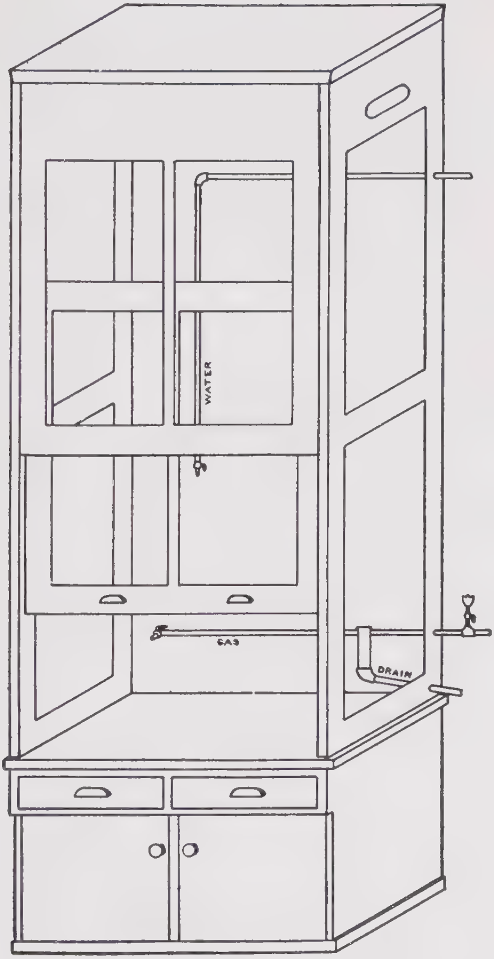

Fig. 87

The entering water should have a temperature approximately that of the room. Since the water obtained from the ordinary pipe system is apt to vary in pressure and temperature, it is desirable to have a permanent tank in the upper part of the room or the cabinet (Fig. 87) that will contain a sufficient supply of water at constant temperature. A large galvanized house-boiler has been found to be satisfactory for this purpose. The thermometers for measuring the temperatures of the inlet and outlet water should be provided with reading glasses, easily movable along the stem, for convenience in reading and the avoidance of errors of parallax. Either Centigrade or Fahrenheit thermometers may be used, but because the results are generally expressed in B.t.u. per cubic foot of gas, a Fahrenheit thermometer and a gas meter reading in cubic feet will be found more convenient. For measuring the temperature of the gas and the products of combustion, thermometers reading to one degree are suitable. Turn on the water, and by means of the cock *19* adjust its rate of flow to a rate of about three pounds per minute. Some of the entering water should overflow continuously through *8* to insure a constant head.

Regulate the gas to flow at the rate of from four to seven cubic feet an hour, admitting enough air to the burner to give a flame with a slightly luminous tip which will insure the perfect combustion of the entering gas and will prevent the cooling of the flame through an excess of air.

Now insert the burner in the combustion chamber and screw it firmly into place in such a position that the base of the flame is not less than one and one-half inches[8] above the lowest level at which the water circulates, and observe with the mirror whether the burner is set in place in the middle of the chamber and whether the gas is burning properly.

The excess of air passing through the calorimeter is controlled by the position of the damper *4*, and the best results are obtained by keeping the excess of air as low as possible while still maintaining complete combustion of the gas. The damper should be set so that the reading of the outlet water thermometer will be at a maximum. The Bureau of Standards[9] recommends as a "normal rate" 70 per cent of that rate at which combustion begins to be incomplete. The determination of the rate at which combustion is no longer complete may be made as follows: Operate the calorimeter until a thermal balance is established on the inlet and outlet water thermometers. Then gradually increase the rate of gas consumption, and as long as combustion is complete the increase of gas rate causes an increase in the outlet water temperature.

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[8] *Bureau of Standards, Circular* No. 48 (1916), p. 47.

Regulate the water supply by means of the cock *19* so that there is a difference of about 15° F. between the temperatures of the entering water and that leaving the calorimeter. Read the thermometer *5* and note whether the escaping gases have approximately the temperature of the room. If they have not, adjust the rates of flow of the water and gas until this result is attained. When the temperatures of the escaping water and of the escaping gases have become constant and the condensed water has begun regularly to drop from the tube *6*, the actual determination of the heating value may be begun.

According to the Bureau of Standards[10] this thermal balance will be established with the Junkers calorimeter in about three minutes.

Determination of the Heating Value of the Gas.—Read and record the prevailing barometric pressure, the temperature of the gas at the meter, the temperature of the room and of the exhaust gases, and the pressure of the gas on the manometer of the regulator. At the moment that the large hand of the gas meter passes the zero mark, note the position of the small hand of the meter and at once turn the three-way cock so that the outlet water flows into the container instead of into the drain. Place a 25 cc. graduated cylinder under the tube *6* to catch the condensed water.

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[9] *Technologic Paper* No. 36 (1914), p. 69.
[10] *Technologic Paper* No. 36 (1914), p. 85.

Then read the inlet and outlet water thermometers *10* and *12*, making the readings as rapidly as possible during the consumption of the gas. At least ten readings should be made of the temperatures of both the inlet and outlet water. When the large hand of the meter passes the zero point the second time, indicating the combustion of two-tenths of a cubic foot of gas, the outlet water is again run into the drain instead of into the container. Then either weigh[11] the water or measure its volume. Measure the volume of the condensate that is collected in the small graduated cylinder to allow the calculation of the net heating value. Again read the temperature of the gas at the meter, the temperature of the room and of the exhaust gases, and the barometric pressure and the pressure shown on the manometer of the regulator. When the tests are completed, turn off the gas and after this has been done, shut off the water.

A duplicate test should be made immediately without disturbing the existing conditions, providing all the readings are within the prescribed limits. The Bureau of Standards[12] reports that the efficiency of this calorimeter is within the limits of experimental error. Allner[13] has described an automatic device with an alarm for shutting off the gas in case the water supply is cut off.

Accuracy of Calorimeters.—The factors affecting the accuracy of determinations of heating value with flow calorimeters have been thoroughly investigated by the Committee[14] on Calorimetry of the American Gas Institute and by the Bureau of Standards.[15] The latter investigation has shown that the accuracy attainable in this determination is affected chiefly by errors in the adjustment of the gas meter, in the measurement of the temperature rise of the water, and in the manipulation of the change-over device, since by proper procedure the errors due to all other factors become nearly, if not completely, negligible. If proper precautions are taken, an accuracy of 0.5 per cent can be secured, and in ordinary routine testing an experienced operator should obtain results accurate to one per cent.

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[11] The weight or contents of the container should be obtained while the inside is wet. This may be done by filling it with water, emptying and shaking in an inverted position for about five seconds. This eliminates any correction when several consecutive tests are made.

[12] *Technologic Paper* No. 36 (1914), p. 114.

[13] *J. Gasbel.*, **56**, 438 (1913).

[14] *Proc. Am. Gas Inst.*, 285 (1908); 148 (1909); 65 (1912).

[15] *Technologic Paper* No. 36 (1914); see also Bunte and Czako, *J. Gasbel.*, **62**, 589 (1919).

Heat of Combustion.—The heating value of a gas containing hydrocarbons will, if it is burned in a closed space, differ from the result obtained when it is burned in the open; this is due to the heat from the condensation of the water and the cooling of the water to room temperature. Consequently in stating the heat of combustion of a substance, it is necessary not only to reduce the volume to some standard conditions, but also to state whether the combustion took place at constant volume or pressure, whether the resulting products were cooled down to the original temperature, and whether the water vapor formed was condensed or the products of combustion were allowed escape at a higher temperature and thus to carry off some heat.

The heat of combustion will be made up of: (1) the heat given up by radiation from the flame and by cooling the products of combustion to the exhaust temperature, and (2) the heat given up by the condensation of the steam.

The Bureau of Standards[16] has defined the heats of combustion as follows:

"The *total heating value* of a gas is the number of British thermal units produced by the combustion, at constant pressure, of the amount of gas which would occupy a volume of one cubic foot at a temperature of 60° F., if saturated with water vapor and under a pressure equivalent to that of 30 inches of mercury at 32° F. and under standard gravity, with air of the same temperature and pressure as the gas, when the products of combustion are cooled to the initial temperature of the gas and air, and when the water formed by combustion is condensed to the liquid state.

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[16] *Technologic Paper* No. 36 (1914).

"The *net heating value* of a gas is the number of British thermal units produced by the combustion, at constant pressure, of the amount of the gas which would occupy a volume of one cubic foot at a temperature of 60° F., if saturated with water vapor and under a pressure equivalent to that of 30 inches of mercury at 32° F. and under standard gravity, with air at the same temperature and pressure as the gas, when the products of combustion are cooled to the initial temperature of gas and air and the water formed in combustion remains in the state of vapor."

The *observed heating value* is the "value obtained by multiplying the mass of water which flowed through the calorimeter during the test by the corrected rise in temperature of the water, and dividing by the volume (referred to the standard conditions of 60° F. and 30 inches) of the gas burned."

Calculation of the Observed Heating Value.—Average the readings of the barometric pressure, the temperature of the room, gas and exhaust gases, and the pressure of the gas on the manometer of the regulator at the beginning and end of the experiment. The barometric reading is corrected for temperature and calibration. (See Chap. III.) The equivalent in inches of mercury of the pressure at the regulator is added to the corrected barometric pressure to give the total gas pressure. The calibration correction should also be applied to the gas temperature at the meter.

Correct the meter readings from the meter calibration constant, and reduce the volume of gas that has been burned to the volume that it would occupy under the above standard conditions with the aid of the formula,

$$v_0 = v\frac{(p - m)(60 + 459.4)}{(t + 459.4)(30 - e)}$$

in which

v_0 represents the volume of the gas, in cubic feet, at 60° F. and 30 inches of mercury, and saturated with water vapor,

v represents the volume of the gas in cubic feet under the prevailing conditions,

p represents the total gas pressure,

m represents the tension of water vapor at t° in inches of mercury (see table on p. 473),

e represents the tension of water vapor at 60° F. in inches of mercury (see table on p. 473),

t represents the temperature of the gas (° F.).

The readings of the inlet and outlet water thermometers are averaged, and corrections are applied to the average readings for the calibration, emergent stem, and differential correction.[17]

The correction for the emergent stem may be computed from the formula

$$\text{Correction} = K \times u(T^\circ - t^\circ)$$

where

K = 0.000085 for Fahrenheit thermometers and 0.000155 for Centigrade thermometers,
u = number of degrees emergent from the bath,
T = temperature of the water,
t = mean temperature of emergent stem.

The observed heating value of the gas may be calculated by means of the formula

$$HV = \frac{WT}{V}$$

where

W = mass of water heated,
T = average difference of the corrected readings of the inlet and outlet water thermometers,
V = corrected volume of gas burned.

If W is expressed in pounds, T in degrees Fahrenheit, and V in cubic feet, the result is B.t.u. per cubic foot. If W is expressed in grams, T in degrees Centigrade and V in liters, the result is calories per liter. In scientific work the heating value of the gas is usually given as calories per liter of dry gas at 0° C. and 760 mm. pressure.

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[17] *Bureau of Standards, Circular* No. 48, p. 58 (1916).

Calculation of Total Heating Value.—In addition to all the corrections applied in the calculation of the observed heating value, corrections must also be applied for the heat loss, including the correction for the effect of the difference between the temperatures of the inlet water and the room, and for the effect of atmospheric humidity in the calculation of the total heating value.

If the inlet water is at room temperature, there will be some heat losses from the calorimeter due to the fact that the average temperature of the surface is above the temperature of the room, and the exhaust gases are not cooled quite to the room temperature. When the temperature rise is from 15° to 20° F., these losses amount to about 0.1 to 0.2 per cent of the total heating value and it is customary to add a correction of one B.t.u. for this heat loss.

If, however, the inlet water is not at room temperature, another correction must be made. This correction is calculated by multiplying the values given in the following table by the difference between the temperatures of the inlet water and the room.

TABLE XVI

Room Temperature °F.	Corrections in B.t.u. per 1°F.	
	Total Heating Value	Net Heating Value
50	0.5	0.4
60	.6	.4
70	.7	.4
80	.8	.4
90	.9	.5
100	1.0	.5

The correction is added if the inlet water is warmer than the room, and subtracted if it is colder. If the difference between the two temperatures is large, the correction factor corresponding to the mean of the two temperatures should be used.

A correction must also be applied for the water vapor in the exhaust gases which always leave the calorimeter saturated with water vapor. The gas which enters the calorimeter will be saturated with water vapor, but the air for combustion, the volume of which will be approximately seven times that of the gas, may vary greatly in humidity. The water vapor formed in excess of the amount remaining in the exhaust gases will condense, which results in a change in volume.

The humidity of the air is determined with a sling or whirling psychrometer (see Chap. XIX). The correction may then be calculated[18] for the heat loss due to the water vapor

TABLE XVII[19]

Corrections, in B.t.u., to be Applied to Observed Heating Values in Calculating Total Heating Values of Illuminating Gas (about 600 B.t.u.)

The tabular corrections are applicable when inlet water, air, gas, and products are all at approximately the same temperature, and when the calorimeter is operated at *normal rate* of gas consumption (see p. 371).

Temperature of Room, etc.	Relative Humidity of Air									
	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
°F.										
40	+2	+2	+1	+1	+1	+1	0	0	0	−1
45	+2	+2	+2	+1	+1	+1	0	0	0	−1
50	+3	+3	+2	+2	+1	+1	0	0	0	−1
55	+3	+3	+3	+2	+1	+1	+1	0	0	−1
60	+4	+4	+3	+2	+2	+1	+1	0	0	−1
65	+5	+4	+4	+3	+2	+2	+1	0	−1	−1
70	+6	+5	+4	+3	+3	+2	+1	0	−1	−2
75	+7	+6	+5	+4	+3	+2	+1	0	−1	−2
80	+8	+7	+6	+5	+4	+3	+1	0	−1	−2
85	+10	+9	+7	+6	+4	+3	+2	0	−1	−3
90	+12	+10	+9	+7	+5	+4	+2	0	−2	−3
95	+14	+12	+10	+8	+6	+4	+2	0	−2	−4

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[18] *Bureau of Standards, Tech. Paper* No. 36, p. 74 (1914).

[19] From *Bureau of Standards, Tech. Paper* No. 36 (1914).

carried out in the exhaust gases over the amount supplied, or more easily from Tables XVII and XVIII. The corrections are in B.t.u.'s and are added where the sign is + and subtracted where it is −.

TABLE XVIII[20]

CORRECTIONS, IN B.t.u., TO BE APPLIED TO OBSERVED HEATING VALUES IN CALCULATING TOTAL HEATING VALUES OF NATURAL GAS (ABOUT 1000 B.t.u.)

The tabular corrections are applicable when inlet water, air, gas, and products are all at approximately the same temperature, and when the calorimeter is operated at *normal rate* of gas consumption (see p. 371).

TEMPERATURE OF ROOM, ETC.	RELATIVE HUMIDITY OF AIR									
	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
°F.										
40	+4	+3	+3	+2	+2	+1	+1	0	0	−1
45	+4	+4	+3	+3	+2	+1	+1	0	0	−1
50	+5	+5	+4	+3	+3	+2	+1	0	0	−1
55	+6	+6	+5	+4	+3	+2	+1	0	−1	−1
60	+8	+7	+6	+4	+3	+2	+1	0	−1	−2
65	+9	+8	+7	+5	+4	+3	+2	0	−1	−2
70	+11	+9	+8	+6	+5	+3	+2	+1	−1	−2
75	+13	+11	+10	+8	+6	+4	+3	+1	−1	−3
80	+15	+13	+11	+9	+7	+5	+3	+1	−1	−3
85	+18	+16	+13	+11	+9	+6	+4	+1	−2	−4
90	+21	+19	+16	+13	+10	+7	+4	+1	−2	−5
95	+25	+22	+19	+15	+12	+8	+5	+1	−2	−6

The total heating value is found by applying the three above-mentioned corrections to the value obtained for the observed heating value.

Calculation of Net Heating Value.—Since in most industrial processes the exhaust gases are not cooled to room temperature, and since this allows the water formed to escape as steam with the loss of heat, it is customary to correct for this and express the corrected value as the net heating value. This will be less than the total heating value by the quantity of heat equal to the latent heat of vaporization, at the temperature of the gas and air, of the water formed in the combustion.

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[20] From *Bureau of Standards, Tech. Paper* No. 36 (1914).

To calculate the net heating value divide the volume of the condensate collected by the volume of the gas burned, reduced to standard conditions. Multiply this value of the condensate per cubic foot by 2.3, which is the amount of heat in B.t.u. required to vaporize one cc. of water at ordinary temperatures, and subtract this from the observed heating value. Also correct the observed heating value for the heat loss and for the error due to the difference between the inlet water temperature and room temperature as was done in calculating the total heating value. The value obtained is the net heating value.

For further details of these calculations the reader is referred to *Circulars* 48 (1916) and 65 (1917) of the Bureau of Standards. Fig. 88 is an illustration taken from these publications of a complete record of a heating value test.

The Bureau of Standards[21] has published a description of this and some other common instruments of the same type, including the Simmance-Abady, Sargent, and Boys.[22] That of Boys is used extensively in Great Britian.

THE DETERMINATION OF THE HEATING VALUE OF LIQUID FUELS

The heating value of some liquid fuels may be determined by dropping the liquid on a small cellulose block[23] and then burning this in the usual manner in a bomb calorimeter. The determination is, however, customarily made with a calorimeter of the *continuous* type, such as that devised by Junkers. This instrument is primarily designed for use with gaseous fuels, but by means of special attachments[24] it may be employed with liquid fuels as well.

Morpurgo[25] gives a formula by which the calorific value of

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[21] *Technologic Paper* No. 36 (1914).

[22] *Proc. Roy. Soc.*, **77** (A) 122 (1906).

[23] See Kellner, *Landwirtschaftl. Versuchsstat.*, **47**, 275 (1896).

[24] Glinzer, *Z. angew. Chem.*, **19**, 1422 (1906); Moss and Stern, *Engineering*, **114**, 729 (1922).

[25] *Chem. Absts.*, **18**, 2797 (1924).

HEATING VALUE TEST RECORD

Place Bureau Stds. Date Oct. 8, 1913 Time 10 a.m. Gas Gtown

Calorimeter No. J1209 Meter No. 6312 Thermometer No.: Inlet 5781A Outlet 5781B

Gas line purged Yes ~~No~~ Meter adjusted Yes ~~No~~ Leak test Yes ~~No~~ Water valve 65 Damper closed

Differential therm. corr'n. det'd Oct. 1, 1913 (date) Last meter calibration Sept. 4, 1913 (date)

	START	END
Temp. of barometer	68°	68°
Barometer reading	29.52	29.51
Certif. corr'n	−.01	
Temp. corr'n	−.10	
Corr'd. barom. height	29.40	
Pressure at meter (inches of water)	1.5	
Equiv. (inches of mercury)	.11	
Total gas pressure	29.51	
Meter therm. reading	68.1	68.3
Certif. corr'n	−.3	
Meter temp.	67.9	
Reduction Factor F	0.963	
Psychrometer wet bulb	53.0	53.0
Psychrometer dry bulb	68.0	68.5
Humidity	35%	
Temp. of products	69	
Time of 1 meter rev.	52″	
Equiv. rate (cu. ft. per hr.)	6.9	

CONDENSED WATER COLLECTED

	TEST 1	TEST 2
Meter reading: start	18.1	19.4
" " end	19.1	20.4
Condensate (cc)	21.6	21.2
" per cu. ft. (60° 30in.)	22.3	21.9
Average A	22.1	

NET HEATING VALUE

Observed heating value average	644
Corr'n for heat loss	+ 1
Reduction to net (A x 2.3)	−51
Net heating value	594

Certified as correct

E. F. M.

Observer

	SERIES NO. 1		SERIES NO. 2		SERIES NO. 3	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Preliminary	67.94	86.54	67.93	86.40	67.90	86.40
		50		45		45
Used in averaging		50		49		48
		43		40		40
		36		43		39
		43		47		43
		54		50		49
	67.93	49	67.93	50	67.90	52
		50		41		50
		50		40		40
		47		48		42
		40		38		45
Supplementary		49		41		46
	67.93	36	67.92	41	67.90	47
Average	67.93	86.46	67.93	86.45	67.90	86.45
Certificate corr'n	−.18	−.25				
Differential corr'n		−.02	−.18	−.19	−.18	−.19
Emergent stem corr'n		+.08				
Corrected temp.	67.75	86.27	67.75	86.26	67.72	86.26
Temp. rise T.	18.52		18.51		18.54	
Water heated W.	6.74		6.74		6.72	
No. of rev. of meter	2					
Meter calib. 1 rev. =	0.1006					
Gas volume V.	0.2012					
Observed heating value $\frac{W \times T}{V \times F}$	644		644		643	
Corr'n for heat loss	+1					
Corr'n for atmos. humid.	+4					
Total heating value	649		649		648	
Average	649 Btu. per cu. ft. (60°, 30 in.)					

FIG. 88

liquid fuels may be calculated from the data obtained by an Engler distillation.

Discontinuous Calorimeters.—Hempel[26] has described a calorimeter for small quantities of gas. The Graefe[27] calorimeter is very similar. The Parr[28] calorimeter consists of two units, and the heating value of the gas is compared with that of a gas of which the heating value is known. In the Doherty[29] calorimeter, the water after leaving the calorimeter enters a tank containing the sample of gas to be tested, and displaces through the burner a volume of gas equal to the volume of the water which has passed through the calorimeter.

Automatic and Recording Gas Calorimeters.—The underlying principle of the Junkers automatic calorimeter is the same as that employed in the other form, but the instrument is made automatic by rendering constant the ratio of the amount of gas burned to that of water passing through the calorimeter, in which case the difference of temperature is a direct measure of the heating value of the fuel. The temperature difference may be measured by a thermocouple,[30] the junctions of which are immersed in the entering and escaping water, or, if the temperature of the inlet water is kept constant, the heating value may be determined from a recording thermometer[31] showing the temperature of the outlet water. Boys[32] has recently described a recording modification of his calorimeter. The recording calorimeter of Bain and Baten[33] utilizes the relation between the temperature of the flame and the calorific power of the gas. The Sarco[34] calorimeter consists of a U-tube filled with oil, one of the arms of which is heated by the combustion of the gas, the other remaining at room temperature. The heating value is shown by the change in the level of the oil.

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[26] *Z. angew. Chem.*, **14**, 713 (1901); *Gasanal. Methoden*, 4th ed. (1913), p. 384; Foerster and Grunert, *Brennstoff Chem.*, **5**, 1 (1924).

[27] *Z. für chem. Apparatenkunde*, **320**, 723 (1906); Pleyer, *J. Gasbel.*, **50**, 831 (1907); *Braunkohle*, **23**, 273 (1924).

[28] *Ind. Eng. Chem.*, **2**, 337 (1910).

[29] *Am. Gas Lighting J.*, **93**, 1128; *J. Gas Lighting*, **112**, 918; *Proc. Am. Gas Inst.*, 116 (1912).

[30] Junkers, *J. Gasbel.*, **50**, 520 (1907).

[31] Cross, *Am. Gas Inst. J.*, **85**, 673 (1906).

[32] *Proc. Roy. Inst.* (Preprint), April 27, 1923; Higgs, *Gas J.*, **171**, 664 (1925); *Gas J.*, **158**, 882 (1922); **159**, 25 (1922); *Nature*, **110**, 251 (1922).

[33] *J. Chem. Ind.*, **25**, 505 (1906).

Probably the most common instrument of this type in use in this country is the Thomas[35] recording gas calorimeter. This instrument furnishes a continuous record of the total heating value of a gas free from any corrections for conditions of measurement. It consists of two separate units; a tank unit (Fig. 89) where the heating value of the gas is measured, and a recorder which contains the instruments necessary for translating the heat measurements into B.t.u.'s and recording them.

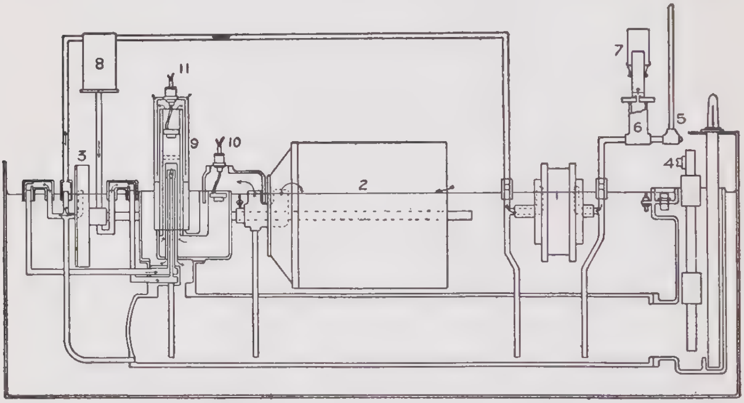

FIG. 89

The operating principle is essentially that of the Junker type except that air instead of water is used as the heat-absorbing medium. This eliminates the necessity of making corrections for variations in room temperature and pressure, because the air and gas are maintained at similar conditions and follow the same physical laws.

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[34] *Proc. Am. Gas Inst.*, **2**, 155 (1912); *J. Gasbel.*, **56**, 381 (1913).

[35] Packard, *Am. Gas Assoc. Monthly*, **2**, 577 (1920); Cutler Hammer Mfg. Co., *Bulletins;* Telghman, *Gas Record*, **17**, 75 (1920); Rogatz and Kowalke, *Ind. Eng. Chem.*, **18**, 1087 (1926).

The wet meter *1* supplies the gas to be tested, the meter *2* supplies the air for absorbing the heat of combustion, and the meter *3* supplies the air for combustion. All of them are geared together and power-driven so that the air and gas are always delivered in fixed volumetric proportions. Any change in water-level affects all their displacements alike, so that the exact water-level within a tenth of an inch is not essential. The water-level is maintained by the pump *4*.

The gas enters the calorimeter through a small orifice *5* and passes into a separator chamber *6* which is open to the atmosphere through a "bleeder" burner *7*. The gas at approximately atmospheric pressure is pumped to the mixing chamber *8*, where it mixes with the air supplied by meter *3*. From there the mixture of air and gas enters the burner *9* where the combustion occurs. A small amount of secondary air is supplied direct to the flame to insure complete combustion. The products of combustion then pass out through the bottom of the burner after having given up their heat to the stream of heat-absorbing air which flows through the burner in a counter direction to that of the combustion gases and is entirely separated from them. The temperatures of the incoming and outgoing cooling air are measured by two resistance thermometers, *10* and *11*, and their difference, which is directly proportional to the total heating value per standard cubic foot of gas (30 inches and 60° F. saturated), is recorded on a chart.

The dilution of the gas with water vapor and the variation in specific heat of saturated air would tend to introduce small errors into this method, but as both errors are a function of the temperature, correction for them is made by using for resistance thermometers nickel wire which has a resistance-temperature relationship which compensates for these effects quite exactly over fairly wide ranges of temperature.

The accuracy of this calorimeter may be checked against a flow calorimeter of the Junker type, or by burning a pure gas of known heating value, such as hydrogen, or with accurate mercurial thermometers.

Calculation of Heating Value.—The heating value of a gas may be determined from its chemical composition if the proportion of each constituent in the gas mixture and the heating values of the constituents are known. In the ordinary analysis of a gas mixture the composition of the olefines is not determined, and an assumption is made for their heating value. When benzene is grouped with the olefines as "illuminants," the possible error in this assumption becomes greater.[36] Therefore unless the actual composition of the olefines is known, only an approximate value can be obtained by this method.

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[36] Weyman, *J. Soc. Chem. Ind.*, **33**, 11 (1924).

CHAPTER XVIII

ACETYLENE

The chief object of the analytical examination of acetylene is the detection and determination of certain impurities in the gas rather than the determination of acetylene itself.

Impurities in Commercial Acetylene.—Commercial calcium carbide may be contaminated with metallic calcium, calcium phosphide, calcium sulphide, aluminum carbide, aluminum nitride, magnesium nitride, or calcium nitride; consequently in the analysis of acetylene the following impurities have to be considered,—hydrogen, ammonia, phosphine, organic compounds of phosphorus, hydrogen sulphide, organic compounds of sulphur, silicon hydride, carbon monoxide,[1] methane (oxygen, nitrogen).

Of these, hydrogen, carbon monoxide, methane, oxygen, and nitrogen need not usually be determined since they are, as a rule, present in only small amounts. They are without appreciable effect upon the luminosity of the acetylene flame, and, if susceptible of oxidation under the prevailing conditions, they yield products that are not objectionable. On the other hand, ammonia, phosphine, organic compounds of phosphorus, hydrogen sulphide, organic compounds of sulphur, and silicon hydride should be tested for and, if found to be present, should be determined, because, upon combustion of the gas, nitric acid is formed from ammonia, phosphoric acid from phosphine and other compounds of phosphorus, sulphurous acid and sulphuric acid from hydrogen sulphide and other compounds of sulphur, and silicon dioxide from silicon hydride. These products of oxidation vitiate the air or attack and clog the metal parts of the burner.

Sampling of Calcium Carbide.—The analyst may at times be called upon to analyze acetylene gas itself, but more often he is given a sample of calcium carbide and is asked to report upon the purity of the acetylene that is evolved from it. As commercial calcium carbide is usually far from uniform in composition, trustworthy results as to the purity of the acetylene that it yields can be obtained only from an average sample[2] that is prepared from a fairly large amount of the carbide. Such a sample of the carbide cannot, however, be prepared in the usual manner by breaking the lumps into small pieces, grinding these to a powder, and mixing the powder. The substance is so hard that considerable time would be required to pulverize the pieces, and during the work the moisture of the air would decompose an appreciable amount of the carbide. The best that can be done under the circumstances is to rapidly break up the carbide into pieces about the size of a pea, to sift these without delay to remove the carbide dust, to then roughly mix the pieces of carbide together, and to place the material thus prepared in dry, tightly stoppered bottles. A sample prepared in this manner is, of course, far from being homogeneous, and for this reason the portion of carbide taken for a determination should amount to about fifty, or even one hundred, grams.

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[1] Keppeler, *J. Gasbel.*, **45**, 804 (1902).

Determination of Hydrogen in Acetylene.—Hydrogen in crude acetylene results from the action of metallic calcium upon the water used to decompose the calcium carbide.

Hydrogen in acetylene may be determined with the Hempel apparatus by absorbing the acetylene with fuming sulphuric acid, oxygen with alkaline pyrogallol, the last traces of acetylene with ammoniacal cuprous chloride, and determining hydrogen (and methane if present) in the residue by combustion.

Determination of Methane in Acetylene.—From the work of Rossel and Sandriset[3] and von Knorre and Arndt,[4] it would appear that there is no methane in acetylene that has been properly generated. If, however, the gas is evolved at high temperature, it may contain considerable amounts of methane.[5] The gas may be determined, together with any hydrogen that may be present in the acetylene, by combustion of the non-absorbable residue.

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[2] See Odernheimer, *Chem. Ztg.*, **26**, 703 (1902).

[3] *Z. angew. Chem.*, 77 (1901).

[4] *Z. d. Ver. z. Förderg. d. Gewerbefleisses*, 162 (1900).

Determination of Oxygen and Nitrogen in Acetylene.—Oxygen and nitrogen may be determined volumetrically by the procedure described under hydrogen, the nitrogen being the gas that remains after the determination of hydrogen and methane.

Determination of Ammonia in Acetylene.—Lewes[6] determines ammonia in crude acetylene by passing the gas through a standard solution of sulphuric acid and titrating the excess of acid with 0.1 N ammonium hydroxide, using litmus as indicator.

Ammonia, however, does not usually occur in sufficient quantity for determination by titration. Very small amounts of it may be determined by passing the crude acetylene through dilute hydrochloric acid, evaporating the solution to dryness to remove the other gases and the excess of acid, and determining the ammonia with Nessler's reagent.

Determination of Phosphine in Acetylene.—Phosphine is almost always present[7] in crude acetylene. It is due to the reaction between calcium phosphide and water. If the acetylene is evolved at high temperature, as is frequently the case when water is allowed to drop upon the calcium carbide, organic phosphorus compounds may also be formed, but if appreciable rise of temperature during the generation of the gas is avoided, the amount of these organic substances is negligible, and all of the phosphorus that is present may be assumed to exist in the form of phosphine.

The amount of phosphine in crude acetylene is quite variable, but it usually lies between .03 per cent and 1.8 per cent.[8]

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[5] Lewes, *J. Soc. Chem. Ind.*, **17**, 533 (1898).

[6] Lewes, *Acetylene* (1900), p. 689.

[7] Vogel, *Handbuch für Acetylen*, p. 232.

[8] Vogel, *loc. cit.*, p. 234. The analyses given by Fraenkel, *J. Gasbel.*, **51**, 431 (1908), show from .024 to .057 per cent by volume of phosphine in crude acetylene.

Since the regulations of the British Acetylene Association allow a permissible maximum of phosphine of 0.5 per cent by volume, it is apparent that the determination of this gas in crude acetylene cannot satisfactorily be accomplished by a volumetric absorption method that uses a sample of only one hundred cc. of acetylene.

Of the methods that have been proposed for the determination of the gaseous compounds of phosphorus in acetylene, the combustion method developed by Eitner,[9] Keppeler,[10] and Fraenkel,[11] and the sodium hypochlorite absorption method of Lunge and Cedercreutz[12] are in most general use. The first of these methods, in which the phosphorus in crude acetylene is determined by burning the gas and ascertaining the amount of phosphoric acid in the products of combustion, gives the total amount of phosphorus, whether it is present in the gas as phosphine or in the form of organic compounds of phosphorus. The acetylene is burned in a suitable burner under a cylindrical glass hood, and the products of combustion are drawn through an oxidizing solution, such as sodium hypochlorite or sodium hypobromite. The resulting phosphoric acid is then determined by precipitation with "magnesia mixture." On account of the difficulty in regulating the pressure of the gas as it comes from the evolution apparatus, Fraenkel recommends that the acetylene from about 50 grams of calcium carbide be collected over a salt solution in a large tubulated bottle. If, however, the acetylene is to be mixed with an equal volume of hydrogen before combustion, as Fraenkel recommends, the containers must be so large as to render them very unwieldy and quite expensive. Moreover, the accuracy of the determination of phosphorus in the gas will undoubtedly be affected by the reaction between the compounds of phosphorus and the confining liquid. Perks[13] burns the acetylene in an ordinary bicycle acetylene lamp enclosed in a glass hood, and absorbs the phosphoric acid in dilute ammonium hydroxide.

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[9] *J. Gasbel.*, **44**, 548 (1901).
[10] *Ibid.*, **45**, 802 (1902).
[11] *Ibid.*, **51**, 431 (1908).
[12] *Z. angew. Chem.*, 651 (1897).
[13] *Analyst*, **49**, 32 (1924).

The method of Lunge and Cedercreutz in which the crude acetylene is passed directly from the generating apparatus through a solution of sodium hypochlorite is to be preferred to the combustion method if it will yield accurate results. The apparatus that was used by these authors is shown in Fig. 90. A weighed amount of the calcium carbide (from 50 to 70 grams) is placed in the flask *B*. The ten-bulb absorption tube *C* is charged with about 75 cc. of a three per cent solution of sodium hypochlorite and is connected to the evolution flask. Water is now allowed to drop slowly from *A* upon the carbide in *B* at a rate of from 6 to 7 drops a minute. The evolution of acetylene will cease in from three to four hours. Air is then drawn through the apparatus to carry over into *C* any acetylene that may still remain in *B*. The contents of the absorption tube *C* is transferred to a beaker and the phosphoric acid in the solution is precipitated by magnesia mixture.

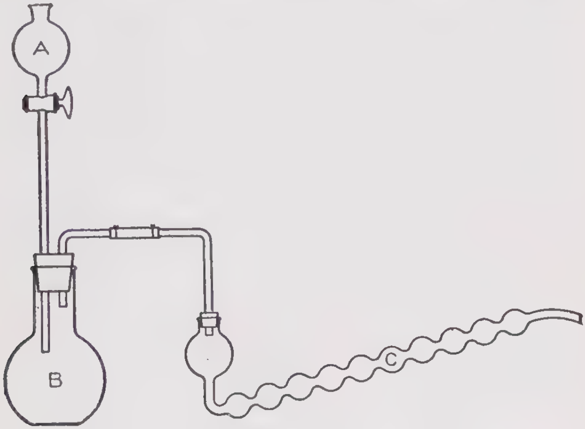

Fig. 90

Objection has been raised[14] to this method because the acetylene is generated by dropping water upon calcium carbide, which is said to give rise to organic compounds of phosphorus that will pass through the solution of sodium hypochlorite without undergoing complete oxidation, and further because of the probable incompleteness of the absorption of the evolved phosphine by the solution of sodium hypochlorite in the ten-bulb tube.

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[14] Eitner and Keppeler, *loc. cit.*

Dennis and O'Brien[15] have improved this by generating the acetylene without appreciable rise in temperature and by using a more efficient absorption apparatus. The evolution of acetylene without marked rise of temperature is accomplished in simple fashion by the employment of a small Kipp apparatus about 40 cm. high, and with bulbs about 10 cm. in diameter. The annular space around the stem between the middle and bottom bulbs is covered with a perforated rubber disk *D* (Fig. 91). A solution of sodium chloride, saturated at room temperature, is poured into the top bulb until the end of the stem in the bottom bulb is covered with the liquid. A perforated stopper carrying a short glass tube is inserted in the neck of the top bulb, the stopper with exit

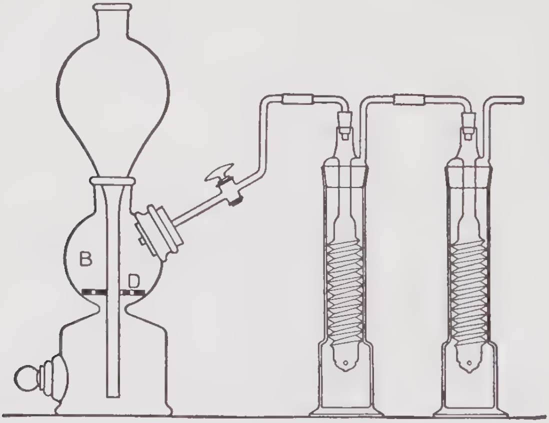

FIG. 91

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[15] *Ind. Eng. Chem.*, **4**, 834 (1912).

tube and glass stopcock is inserted in the tubulus of the bulb *B*, and the further end of the outlet tube is connected with the absorption apparatus that contains the solution of sodium hypochlorite. Hydrogen gas is now passed into the upper bulb of the Kipp generator and through the absorption apparatus to displace the air. About 50 grams of the calcium carbide under examination, broken into pieces about the size of a pea and sifted to remove the dust, is placed in a dry weighing tube and this is at once tightly stoppered and weighed. When practically all of the air has been displaced from the Kipp apparatus by hydrogen, the stopper in the tubulus of the bulb *B* is removed, the contents of the sample tube is poured into the bulb and the stopper is at once reinserted. The current of hydrogen through the apparatus is continued for about one minute, the stopcock is then closed, and the stopper and tube are removed from the upper bulb of the Kipp generator. An additional amount of salt solution sufficient to cause the apparatus to function as a gas generator is then introduced into the upper bulb. The stopcock is now opened to such an extent that the evolved gases pass through the apparatus at a rate slightly faster than will permit of the bubbles being counted. Under these conditions the decomposition of a sample of 50 grams will be effected in about two hours. The reaction between the salt solution and the calcium carbide proceeds at a uniform rate, and with no appreciable rise of temperature.

The absorption apparatus that is employed is a Friedrichs gas washing bottle (see p. 119) modified in form so that the apparatus can easily be rinsed out with water at the close of the run. The solution of sodium hypochlorite with which the absorption apparatus is charged is prepared by dissolving 15 grams of sodium hydroxide in 100 cc. of water, saturating the ice-cold solution with chlorine, driving out the excess of chlorine with a current of air, and then determining the amount of sodium hypochlorite in the solution by treatment with hydrogen peroxide in a Lunge nitrometer (see p. 422).

The solution is then diluted to three per cent NaClO, and about 75 cc. of this solution is placed in each bottle.

After the decomposition of the calcium carbide is complete, the acetylene that remains in the generator is driven over into the absorption bottles by again passing hydrogen through the apparatus in the manner above described. The contents of the gas washing bottles is transferred to a beaker, the bottles and inner tubes being thoroughly rinsed with distilled water. 10 cc. of concentrated hydrochloric acid is added to the liquid which is then boiled until the odor of chlorine is no longer noticeable. Ammonium hydroxide is added to alkaline reaction and the phosphoric acid that is present is determined by precipitation with magnesia mixture, and weighing as magnesium pyrophosphate.

Determination of Volume of Acetylene Evolved from Sample of Carbide.—It is customary to report the results as the per cent by volume of phosphine in the evolved acetylene. This necessitates the determination of the volume of gas that is liberated by the calcium carbide under examination. The most convenient method for making this determination is that proposed by Bamberger[16] who places a definite amount of the carbide in a weighed two-neck Wolff bottle of about 400 cc. capacity, and runs in upon the carbide an amount of a saturated solution of sodium chloride sufficient to entirely decompose the substance. The whole apparatus is weighed before and after the reaction, and the loss in weight equals the weight of the evolved gas which is here assumed to consist entirely of acetylene. The total weight of the Bamberger apparatus before the decomposition of the carbide amounts to from 550 to 800 grams. This weight may materially be reduced by employing, in place of the Wolff bottle, an Erlenmeyer flask of about 250 cc. capacity. This is fitted with a two-hole rubber stopper into one opening of which is inserted the stem of a small separatory funnel of 125 cc. capacity; the other opening of the stopper carries a U-tube filled with calcium chloride. A sample of the calcium carbide amounting to about 50 grams is placed in a weighing bottle, is accurately weighed, and is then introduced into the flask. The stopper carrying the separatory funnel and the U-tube is then inserted, and the funnel is filled with a 20 per cent solution of sodium chloride. The whole apparatus is then weighed on a balance accurate to 0.01 gram. The total weight of this modified form of the Bamberger device is approximately 300 grams. The salt solution is now allowed to drop slowly upon the calcium carbide, and, after decomposition is complete, dry air is passed through the apparatus to expel all of the acetylene. The apparatus is then again weighed, the difference between the two weighings giving the weight of the acetylene evolved. One kilogram of chemically pure calcium carbide yields 405.93 grams of acetylene, equivalent to 348.4 liters of acetylene under standard conditions. Assuming that the loss of weight in the apparatus equals the weight of the acetylene evolved, the volume of the liberated gas may be calculated from the data obtained.

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[16] *Z. angew. Chem.*, 196 (1898).

Determination of Sulphur in Acetylene. — The determination of sulphur in acetylene may conveniently be combined with the determination of phosphine (see under Phosphine, p. 387). The sodium hypochlorite solution oxidizes compounds of sulphur to sulphuric acid. Phosphoric acid that is simultaneously formed is precipitated by magnesia mixture that is free from sulphates. After the ammonium magnesium phosphate precipitate has been removed by filtration, the filtrate is acidified with hydrochloric acid, heated nearly to boiling, and the sulphuric acid precipitated with barium chloride. It has been claimed by some that this method does not oxidize all of the sulphur compounds in the gas, and that accurate results will be obtained only when the crude acetylene is burned and the sulphuric acid is determined in the combustion products.

Determination of Silicon Hydride in Acetylene.—This gas may be determined by the method of Fraenkel[17] which consists in burning crude acetylene under a cylinder of glass, or better of platinum, rinsing out the cylinder with hydrochloric acid, and determining the silica that has resulted from the combustion.

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[17] *J. Gasbel.*, **51**, 433 (1908).

Determination of Carbon Monoxide in Acetylene.—Keppeler[18] determines carbon monoxide in crude acetylene by absorbing the acetylene with fuming sulphuric acid in a Hempel pipette, and treating the gas residue with potassium hydroxide, bromine, and phosphorus. There was a further absorption when the residual gas was passed into a pipette containing a solution of cuprous chloride. Assuming that this absorption was due entirely to carbon monoxide, he found that the amount of that gas was about 0.02 per cent of the crude acetylene.

Lundström,[19] however, found as much as 1.48 per cent of carbon monoxide in acetylene, and Caro[20] as high as 2.3 per cent.

[18] *J. Gasbel.*, **45**, 802 (1902).
[19] *Chem. Ztg.*, **23**, 180 (1899).
[20] *Z. Calc. und Acet.*, **1**, 337 (1898).

CHAPTER XIX

EXAMINATION OF ATMOSPHERIC AIR

Composition of Atmospheric Air.—The normal constituents of the atmosphere are nitrogen, oxygen, the gases of the argon group, carbon dioxide and water vapor. These substances, with the exception of water vapor, are present in nearly constant amount in air that is free from local contamination. The composition[1] of dry air in per cent by volume at sea-level is:

Nitrogen	78.03
Oxygen	20.99
Argon	0.94
Carbon dioxide[2]	0.03
Hydrogen	0.01
Neon	0.00123
Helium	0.0004
Krypton	0.00005
Xenon	0.000006

Local conditions may, however, give rise to the presence in air of such substances as ammonia, nitrous acid, nitric acid, sulphur dioxide, sulphuric acid, carbon monoxide, soot,[3] ozone,[4] etc. The possibility of the presence of these and other occasional constituents in the atmosphere renders it necessary to adopt such methods in the examination of air as will meet the demands of the special case in hand. The determination of most of the substances enumerated above is discussed in Chapter XIV. Two constituents, however, water vapor and carbon dioxide, deserve special consideration because almost every examination of air from a sanitary standpoint involves the determination of these two substances. Many methods for rapidly and accurately determining these constituents of the atmosphere have been developed, and a few of the more satisfactory procedures thus far devised will here be described.

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[1] *International Critical Tables,* Vol. I, 393 (1926).

[2] See also Johnston and Walker, *J. Am. Chem. Soc.*, **47**, 1807 (1925).

[3] Cohen and Ruston, *J. Soc. Chem. Ind.,* **30**, 1360 (1911).

[4] See p. 189.

A very complete discussion of the history of air analysis, and of the amounts of oxygen and carbon dioxide in the atmosphere, has been given by Benedict.[5]

DETERMINATION OF MOISTURE IN THE ATMOSPHERE

Absolute and Relative Humidity.—Water vapor is always present in atmospheric air, but the amount varies greatly. The maximum quantity of water vapor that can be present in any given space is dependent upon the prevailing temperature but is independent of the amount of air in that space. When this maximum quantity of water vapor is present, the space is said to be saturated with water vapor. The quantity of water vapor existent in a given space, such as a cubic foot or a cubic meter, is termed the "absolute humidity" and may be expressed in terms of its weight (in grains or grams) or of its pressure (in inches or millimeters of mercury). The ratio between the amount of water vapor actually present in a given space and the maximum quantity of the vapor that could exist in that space at the observed temperature is termed the "relative humidity." It is usually expressed in per cent of the maximum humidity.

Wet and Dry Bulb Thermometers.—Of the large number of methods that have been devised for the determination of the amount of water vapor in air, one of the most satisfactory is that employed by the Weather Bureau of the United States Department of Agriculture. It is based upon the facts that water will evaporate as long as the adjacent space is not saturated with water vapor, and that this evaporation is accompanied by the absorption of heat. Consequently, if two thermometers are exposed to the air and a moist cloth is placed around the bulb of one of them, this "wet bulb" thermometer will show a lower temperature than the "dry bulb" thermometer unless the surrounding space is saturated with water vapor. The less the amount of moisture in the air, the greater will be the drop in temperature of the wet-bulb thermometer. From the final readings of the two thermometers the amount of water vapor then present in the air may be calculated.

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[5] *The Composition of the Atmosphere.* Publication No. 166 of the Carnegie Institution of Washington, 1912. See also Tower, *J. chim. phys.*, **11**, 249 (1913); Leduc, *Compt. rend.*, **160**, 710 (1915); Boothby and Sandiford, *Am. J. Physiol.*, **55**, 295 (1921).

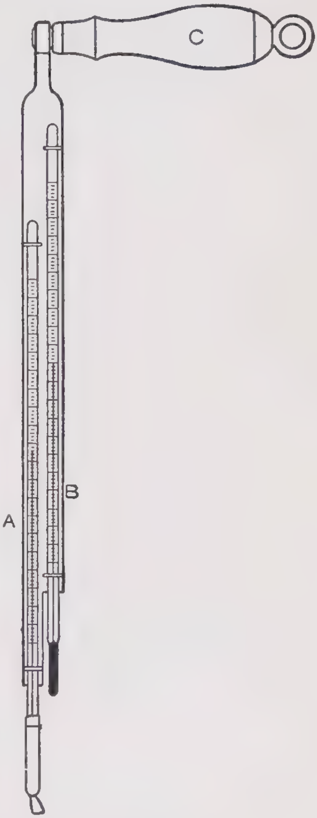

FIG. 92

Psychrometers. — The instruments employed by the Weather Bureau for this work are the sling psychrometer, Fig. 92, and the whirling psychrometer, Fig. 93. They consist of two thermometers, *A* and *B*, which are so mounted that they can be whirled. The bulb of one thermometer (the "wet bulb") is covered with a piece of thin muslin that should first be washed to remove sizing. A small rectangular piece of the washed muslin, wide enough to go about one and one-third times around the bulb, and long enough to cover the bulb and a part of the stem above the bulb, is thoroughly moistened with distilled water and is neatly fitted around the thermometer. It is first tied around the upper end with a piece of strong thread. A loop of thread is next passed around the lower end where it projects beyond the bulb, and the thread is then drawn tightly around the muslin in a knot close up to the lower surface of the bulb and the knot is secured. If this is properly done the muslin will be neatly stretched over the bulb and securely fastened at the bottom.[6]

Manipulation of the Psychrometer.—In making a determination of atmospheric moisture, the "wet bulb" is dipped into a cup of pure water to thoroughly saturate the muslin with water. The thermometers are rapidly whirled for from

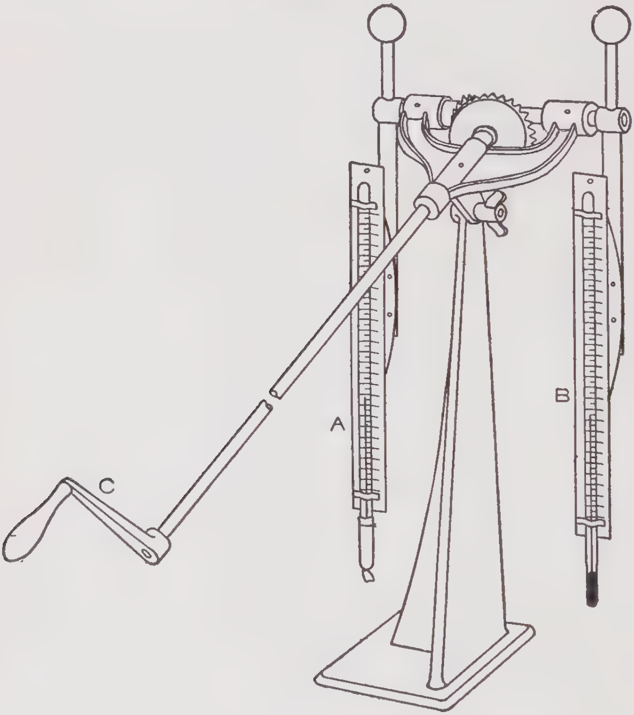

Fig. 93

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[6] See U. S. Dept. of Agriculture, *Weather Bureau Bulletin* No. 235, p. 5 (1915).

fifteen to twenty seconds. The whirling is stopped, and the two thermometers are quickly read, the "wet bulb" thermometer being first read. They are immediately whirled again and a second reading is taken. This is repeated until two successive readings of the "wet bulb" agree very closely, which shows that the thermometer has reached its lowest temperature. The thermometers must usually be whirled a minor more before this temperature is reached.

The rate of evaporation of the water surrounding the "wet bulb" will vary as the movement of the air past the bulb varies, and for these reasons accurate results cannot be obtained unless the speed of passage of the air by the bulb is rapid and uniform. It is for this reason that the thermometers are whirled. The whirling should not be too fast, but should be carried on at such rate that the bulb of the thermometer will have a velocity of about fifteen feet per second.

Calculation of Results.—In the calculation of results the following equation is employed:

$$e = e' - 0.000367P(t - t')\left(1 + \frac{t' - 32}{1571}\right)$$

in which e is the absolute humidity in inches of mercury, t and t′ are the temperatures respectively of the "dry" and "wet bulb" thermometers expressed in degrees Fahrnheit, P is the barometric pressure of the air in inches of mercury and e′ is the maximum tension of water vapor in inches of mercury at the temperature t′ of the "wet bulb."

It would seem preferable, in scientific work, to express the temperatures in degrees Centigrade, and the barometric pressure in millimeters of mercury. If this be done the formula becomes

$$e = e' - .000661B(t - t')\,\frac{(873 + t')}{873}$$

in which B is the barometric pressure in millimeters of mercury, and t and t′ are the temperatures of the wet and dry bulb thermometers in degrees Centigrade.

The absolute humidity e having thus been ascertained, the *relative humidity* is calculated by dividing this result by the maximum tension of water vapor E possible at the temperature shown by the dry bulb thermometer. This result multiplied by 100 gives the relative humidity expressed in "degrees" or per cent.

$$\begin{matrix}\text{Relative humidity in}\\ \text{degrees or per cent}\end{matrix} = \frac{e}{E} \times 100$$

The values of E at temperatures between $-2°$ and $+34°$ C. will be found on page 471.

The United States Weather Bureau in *Bulletin No. 235* gives complete psychrometric tables by means of which, if the temperatures of the wet and dry bulb thermometers and the barometric pressure are known, the relative humidity may be read off directly.

Wheeler[7] and Behr[8] have described an automatic humidity recorder working on this same principle. The air is drawn over wet bulb and dry bulb resistance thermometers which are connected to a Leeds and Northrup recorder so as to give a continuous record of the relative humidity.

Somewhat simpler instruments than the sling or whirling psychrometer, but which are based upon the same principle, are those that consist of two thermometers placed side by side on a stand. The bulb of one of the thermometers is covered with thin muslin that is kept moist by a small lamp-wick which is fastened over the muslin and dips into a vessel that contains water. Evaporation is allowed to proceed until the temperature of the wet bulb ceases to fall. The temperature of this thermometer, t', is then read, and also that of the dry thermometer, t. The absolute humidity of the air is then calculated with the use of the formula,

$$e = e' - k\ (t - t')\ b$$

in which e' is the tension corresponding to the temperature t', and b is the barometric pressure in millimeters. k is an empirical factor that varies with the speed of flow of the air past the wet bulb. According to the researches of Regnault, the values for k under different conditions are as follows:

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[7] *Bell System Tech. J.*, **3**, 238 (1924).

[8] *J. Opt. Soc. Am.*, **12**, 623 (1926).

In small closed rooms	0.00128
In large closed rooms	0.00100
In halls with open windows	0.00077
In courts	0.00074
In open air (no wind)	0.00090

It is not always easy, however, to decide which factor should be used, and experience has shown that these instruments will yield satisfactory results only when they are standardized against the sling or whirling psychrometer, and the proper factor for the special surroundings is thus determined.

These instruments are also made in the recording type,[9] but the pen recorders are usually not satisfactory[10] because the wet bulb is not properly ventilated.

A convenient modification of the psychrometer is the "Hygrodeik." By means of a pointer and chart attached to this instrument, the relative humidity of the atmosphere may be read off with ease and celerity.

Other Instruments.—In addition to the psychrometers, three other methods[11] may be used for the determination of the moisture in the atmosphere. In the chemical method, the moisture is absorbed and weighed, or it may be absorbed with concentrated sulphuric acid as in the Rudorff apparatus.[12] The moisture may also be determined from the temperature of condensation as in Regnault's dew point apparatus.[13] The third method is based upon the change in length of a hygroscopic material,[14] as in the hair hygrometers.

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[9] *Met. Chem. Eng.*, **11**, 725 (1913).

[10] Wheeler, *loc. cit.*

[11] Fergusson, *J. Optical Soc. Am.*, **10**, 119 (1925).

[12] Rideal and Hannah, *Analyst*, **40**, 48 (1915).

[13] U. S. Department of Agriculture, *Weather Bureau Bulletin* No. 235 (1915).

[14] Crockatt and Forster, *J. Soc. Chem. Ind.*, **38**, 95 (1919).

DETERMINATION OF CARBON DIOXIDE IN THE ATMOSPHERE

The deleterious effects that result from the breathing of air in crowded or ill-ventilated rooms have, in the past, been supposed to be due to poisonous substances exhaled from the lungs of the occupants. Inasmuch as it has been impossible to ascertain the quantity of these emanations from the lungs, the carbon dioxide, which is simultaneously exhaled and which can be accurately determined, has been regarded as a measure of the toxic organic substances.

It is now believed that the injurious effects arising from poor ventilation are due not to toxic emanations from the lungs, but rather "to a disturbance of the normal thermal relations of the body. It is a common observation that the depression and fatigue experienced on a hot, humid August day are very similar to the feelings that develop in a crowded 'close' room. The cause is apparently the same in both cases, namely, interference with the normal rate of loss of body heat. At least three atmospheric factors may be concerned in such interference: high temperature of the ambient air, high moisture content and lack of air movement. Paul[15] kept healthy persons for several hours in a close cabinet until the carbon dioxide rose to 100 or 150 parts per thousand—more than ten times the amount usually stated as 'allowable'—but so long as the temperature and moisture content were kept low, no symptoms of illness or discomfort developed. Other experimenters have reached the same result by simply having electric fans whirled in such an experiment cabinet. The motion these imparted to the air was sufficient to facilitate a normal, physiologic loss of heat from the body in spite of high temperature and humidity. Similar cabinet experiments in which the subject was enabled to breathe the fresh outside air through a tube, but was otherwise subjected to the conditions of a close room, likewise showed that the symptoms attributed to 'bad ventilation' are in nowise due to poisons excreted in the breath. The upshot of all such experiments is that it is not the chemical constitution of indoor air that is injurious, but the overheating, the stagnation and sometimes the moisture content." [16]

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[15] Paul, *Z. Hyg.*, **49**, 405 (1905).

It still remains true, however, that the amount of carbon dioxide in the air of a room furnishes a means of judging the efficiency of the ventilation, and for this reason the accurate determination of this constituent is still of importance even although it appears that the accompanying exhaled products from the lungs are not toxic in character.

According to Benedict,[17] the amount of carbon dioxide in air serves as quite an exact indication of the per cent of oxygen that is present. "For every 0.01 per cent increase in the atmospheric carbon dioxide, one may safely assume a corresponding decrease in the percentage of oxygen."

Methods Employed in Determination of Carbon Dioxide in Air.—The methods that have been devised for the determination of carbon dioxide in the atmosphere may roughly be divided into two classes: those in which the carbon dioxide is absorbed by a suitable solution of known strength, and the excess of the absorbent is determined by chemical means; and those in which the carbon dioxide is absorbed and the consequent decrease in the volume of the sample of air is measured.

THE HESSE METHOD.—A great number of methods of the first class have been proposed. Most of them aim to give approximate results [18] in a short space of time. These will not here be considered. Of the other and more accurate methods, that original with Saussure and improved by Pettenkofer and later by Hesse [19] has proved itself to be one of the most satisfactory.[20]

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[16] *Jour. Amer. Med. Assoc.*, **57**, 980 (1911).

[17] *The Composition of the Atmosphere.* Publication No. 166 of the Carnegie Institution of Washington (1912), p. 115.

[18] Cohen and Appleyard, *Chem. News*, **70**, 111 (1894); Doherty, *ibid.*, **109**, 281 (1914); Higgins and Marriott, *J. Am. Chem. Soc.*, **39**, 68 (1917); Bieler, *Chem. Ztg.*, **47**, 893 (1923).

[19] *Anleitung zur Bestimmung der Kohlensäure in der Luft, nebst einer Beschreibung des hierzu nöthigen Apparates;* Eulenberg's *Vierteljahrsschr. f. gerichtl. Medicin und öffentl. Sanitätswesen*, N. F. **31**, 2.

[20] Rauch, *Chem. Absts.*, **16**, 35 (1922).

In this procedure the carbon dioxide in a known volume of air is absorbed by a solution of barium hydroxide of known strength and the amount of barium hydroxide that has not combined with carbon dioxide is then determined by titration with a solution of hydrochloric acid, phenolphthalein being used as indicator.

Solutions Used in the Hesse Method.—The stock solutions needed in the analysis are the following:

(1) A standard solution of hydrochloric acid approximately 0.1 *N*. This solution may be standardized by precipitation as silver chloride or by titration against pure sodium carbonate.

(2) A dilute solution of barium hydroxide, approximately 0.03 *N*, prepared by dissolving 5 grams of a mixture of barium hydroxide and barium chloride (20:1) in one liter of distilled water. This is placed in a bottle *B* (Fig. 94), provided with a small absorption bottle *C* that contains sodium hydroxide which frees the entering air from carbon dioxide. Phenolphthalein is added to this solution until it has a faint but distinct pink color.

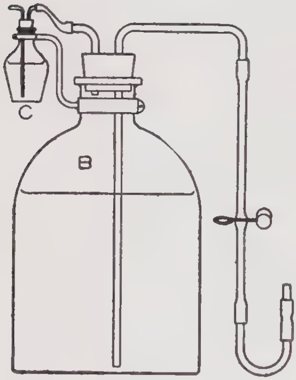

FIG. 94

(3) A solution of phenolphthalein[21] that contains one part of the substance dissolved in 250 parts of alcohol.

Collection of Samples of Air.—The samples of air are collected in thick-walled Erlenmeyer flasks of 100, 200, 300, 400, 500 cc. capacity that are supplied with tightly fitting, double-bore rubber stoppers. The point to which the rubber stopper reaches into the neck of the flask is marked on each flask, and the capacity of the flask up to this line is determined and is marked on the glass. Pieces of glass rod from 3 to 5 cm. long are used to close the openings in the stoppers. These rods should be well rounded at the lower ends and should be widened at the upper end by heating them in the flame of a blast lamp and pressing them on a cold surface. Further apparatus that is needed in the work comprises a pipette of 10 cc. capacity, and a burette with glass stopcock. The burette has a capacity of from 10 to 15 cc., is graduated in 0.1 cc., and has a tip about 8 cm. long.

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[21] Moir, *Chem. Absts.*, 7, 3092 (1913), recommends the use of benzaurine or thymolphthalein.

Manipulation.—Each determination of carbon dioxide by Hesse's method is in reality a double one, two determinations of the constituent being made in samples of air of different volumes. These samples are collected in two of the Erlenmeyer flasks above described, the two flasks being different capacity and the sizes of the flasks that are used depending upon whether a small or a large amount of carbon dioxide in the air is to be expected. The samples of air are collected by completely filling the flasks, at the place where the air is to be examined, with distilled water that has the same temperature as the surrounding air, and then pouring out the water and immediately inserting the rubber stoppers in the necks of the flasks, the holes of the stoppers being closed with the glass plugs.[22] In this operation care should be exercised that the flask is not warmed by the hand and that no air exhaled by the operator enters the flask. The flasks are transferred to the laboratory and the carbon dioxide in each of the two samples is then determined. The glass plug is removed from the end of the rubber tube (Fig. 94), the tip of the 10 cc. pipette is inserted into the end of the tube, the pinchcock is opened and some of the solution of barium hydroxide is drawn up into the pipette. The pipette is rinsed with this solution which is then driven out of the pipette. The pipette is then reinserted in the end of the rubber tube and barium hydroxide is drawn up to the zero mark whereupon the pinchcock is closed. One of the glass plugs in the stopper of one of the Erlenmeyer sample flasks is withdrawn and the tip of the pipette is inserted into the flask through this opening. The solution of barium hydroxide is then run into the flask, the air that is displaced by the solution being allowed to escape by momentarily removing the glass plug in the other hole of the stopper. The last drops of barium hydroxide in the pipette are driven out by closing the upper end of the pipette with the finger, and warming the wider portion of the pipette with the hand. The pipette is then withdrawn from the flask and the stopper is closed with the glass plug. This procedure is repeated with the other sample of air contained in the second flask. The closed flasks are allowed to stand for from fifteen to twenty minutes[23] with occasional shaking. For the complete absorption of the carbon dioxide in the sample of air in the flask it is essential that the barium hydroxide be present in so large excess that not more than one-fifth of it enters into the reaction.

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[22] Grozea, *Chem. Absts.*, **10**, 438 (1916), describes a method of transferring a sample of air to the Erlenmeyer flask at atmospheric pressure.

While the absorption of carbon dioxide in the flask is proceeding, the strength of the solution of barium hydroxide is determined by filling the burette to the mark with the dilute, standardized solution of hydrochloric acid, inserting the tip of the burette through one opening of a two-hole rubber stopper, placing the stopper in the neck of a 100 cc. Erlenmeyer flask in the manner shown in Fig. 95, and then running into the flask a volume of the solution of hydrochloric acid almost sufficient to neutralize 10 cc. of the solution of barium hydroxide. 10 cc. of this latter solution is then introduced into the flask in the manner above described, and hydrochloric acid is carefully added until the pink color of the indicator just disappears. If the color reappears on standing, it should be disregarded.

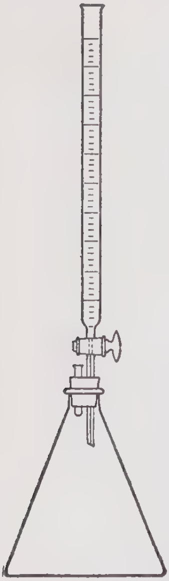
Fig. 95

The excess of barium hydroxide in the two sample flasks is then titrated by filling the burette to the mark with the standardized, dilute hydrochloric acid, inserting the tip of the burette through one of the openings of the stopper and running in the hydrochloric acid at first rapidly, and then toward the end of the reaction drop by drop. The increase of pressure in the flask is relieved from time to time by momentarily lifting the glass plug in the other opening of the stopper. As before, the end point of the reaction is the first disappearance of the pink color.

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[23] Johnston and Walker, *J. Am. Chem. Soc.*, **47**, 1814 (1925), state that with vigorous shaking the absorption is complete in two minutes.

Calculation of Results.—The temperature and the prevailing atmospheric pressure are then read. 10 cc. is deducted from the volume of each sample flask to allow for the volume of air displaced by the solution of barium hydroxide that has been introduced, and the remaining volume is corrected to standard conditions of temperature and pressure. This result represents the volume of the air sample in the flask. The number of cubic centimeters of the solution of hydrochloric acid required to neutralize the excess of the barium hydroxide is deducted from the volume of hydrochloric acid required to neutralize 10 cc. of the barium hydroxide. Representing this difference by n, the amount of carbon dioxide in the sample may be calculated as follows:

$$\frac{\text{n} \times \text{normality of the HCl} \times .044}{2 \times .0019768} = \text{volume of carbon dioxide in the sample in cc.}$$

$$\frac{\text{Volume of } CO_2 \times 10{,}000}{\text{Volume of air sample taken}} = \text{parts of carbon dioxide per 10,000 of air.}$$

Several modifications of this method have been proposed. Freund[24] absorbs the carbon dioxide in a mixture of barium chloride and sodium hydroxide or in sodium hydroxide alone, and titrates the excess of alkali with sulphuric, hydrochloric, or oxalic acid, using phenolphthalein. Lundegardli[25] has described a modified apparatus, and Johnston and Walker,[26] after the absorption of the carbon dioxide in barium hydroxide, filter off the barium carbonate without contact with the air, running the barium hydroxide into an excess of hydrochloric acid. The excess of hydrochloric acid is then titrated with barium hydroxide.

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[24] *Chem. Absts.*, **16**, 36 (1922).

[25] *Biochem. Z.*, **131**, 109 (1922).

THE PETTERSSON-PALMQVIST METHOD.—Of the second type of methods for the determination of small percentages of carbon dioxide, that devised by Pettersson and Palmqvist[27] is one of the most satisfactory and accurate.

The apparatus that they designed permits of the measurement of as small a volume of air as 25 cc. with an accuracy of one part in 10,000, and avoids the necessity of making corrections for variations in pressure and temperature. This is made possible by the use of a compensating tube that is filled with air and that stands in communication with one side of a manometer tube, the burette in which the air is measured being attached to the other side of the manometer. Both compensating tube and burette, which are of nearly the same capacity, stand in a vessel of water. If the temperature of this surrounding water changes during the experiment the effect upon the volume of air in each tube is the same.

If, now, the two tubes are always brought into communication with the manometer when the air in the burette is measured, it follows that if the liquid in the manometer is brought to the same point in each case, the air in the burette is measured under exactly the same conditions of pressure and temperature as prevail in the compensating tube, and since the inclosed volume of air in the compensating tube, which is of course unaffected by changes in barometric pressure, is at each measurement brought back to the volume corresponding to the original conditions of temperature and pressure, the air in the burette is similarly affected, and for this reason no corrections for changes in temperature and pressure are necessary.

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[26] *J. Am. Chem. Soc.*, **47**, 1807 (1925).
[27] *Ber.*, **20**, 2129 (1887).

The apparatus of Pettersson and Palmqvist, with slight modifications introduced by one of the authors (D) is shown in Fig. 96. The air is measured in the burette *A* which contains 25 cc. from a mark on its upper capillary tube down to the zero point at the lower end of the capillary *S*. This capillary is graduated in divisions each of which amounts to 0.0001 part of the total volume of the burette. The somewhat wider capillary *T* is graduated in divisions that represent 0.001 part of the volume of the burette. The lower end of *T* is connected by means of a piece of rubber tubing with the glass stopcock *V;* this rubber tube can be compressed by turning the screw *N* and forcing down upon the tube a flat metal plate attached to the end of the screw. The lower tube of the stopcock *V* is joined to the level-bulb *E* by a piece of "varnished" rubber tubing. At the upper end of the burette *A* are three branch capillary tubes. The one to the left in the drawing is provided with the two-way stopcock *J* through which the sample of air is drawn into the apparatus either directly from the outer atmosphere through *P* or through the coil of copper tubing *H* and the glass tube *I*. At the right, *A* is connected through the stopcock *L* with an Orsat gas pipette *B* that contains glass tubes and is charged with a solution of potassium hydroxide for the absorption of carbon dioxide. The other branch capillary tube joins *A* through the stopcock *K* to the manometer *M* which may be brought into communication with the outer air by opening the stopcocks *F* and *G*. The other end of *M* is connected by the rubber tube *D* to the glass compensating tube *C*. The burette *A*, the pipette *B*, the compensating tube *C* and the coil of copper tube *H* as well as the capillary tubes *S* and *T* are surrounded by water that is contained in the wide glass cylinder and in the jacket tube around the lower capillaries. The whole apparatus is mounted on a board about 90 cm. high and 30 cm. wide which is itself set into a square wooden base. The apparatus can be covered by a wooden box that slides down over it and that is held in place by the screws shown at the top of the board.

The manometer M contains a drop of petroleum in which azobenzene is dissolved, and there is etched upon the surface of the tube a scale by means of which the position of the drop may be read.

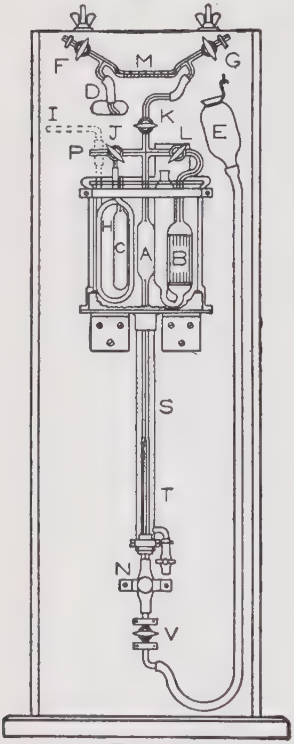

Fig. 96

The coil of copper tube *H* has been added to the original Pettersson-Palmqvist apparatus because it has been found, in determining the carbon dioxide in the air of rooms that are or recently have been occupied, that it takes several minutes for the sample of warm air from the upper part of the room to fall to the temperature of the water that surrounds *A*. This is shown by the side movement of the drop of liquid in the manometer after the sample has been measured. If, however, instead of drawing the air directly into *A* through *P* it is caused to pass through the coil *H*, which is about 80 cm. long, 3 mm. internal diameter, and 5 mm. external diameter, the entering sample of air is rapidly cooled (or warmed) to the temperature of the surrounding water.

It has oftentimes been noticed that the change in the volume of the sample of air in *A* that is caused by its rising or falling to the temperature of the surrounding water, produces a greater movement of the manometer liquid than would result from the removal of the carbon dioxide in the sample.

In making a determination of carbon dioxide with this apparatus, clean mercury is poured into the level-bulb *E* in an amount sufficient to fill the connecting tubes and the burette *A*. The stopcock *J* is turned to such position that *A* communicates with *P*, and one drop of water is introduced into the end of the tube and is drawn over into *A*. The absorption tube *B* is then filled with a 33 per cent solution of potassium hydroxide. The apparatus is now transferred to the place where the air or other gas mixture is to be examined. The glass cylinder surrounding the absorption and measuring tubes is filled with water of the temperature of the surrounding air. Stopcocks *V* and *J* are now opened, the level-bulb *E* is raised, and mercury is driven nearly to the top of the burette *A*. *J* is now closed, the level-bulb *E* is lowered, the stopcock *L* is carefully opened, and the solution of potassium hydroxide in the absorption tube *B* is drawn up to a mark on the stem at which this solution must always stand when measurements are made. *L* is then closed, *J* is turned to such position that *A* communicates with *P* and the mercury in the burette *A* is raised until it stands at the mark on the capillary tube above the burette. The level-bulb *E* is now slowly lowered, and air is drawn into *A* until the mercury falls to about the point *T*. *J* is then turned to such position that *A* communicates with the coil *H* and the level-bulb is now raised and this first sample of air is driven out through the outlet *I*. A second sample is now drawn in through *I* and *H* by lowering *E*, the mercury being allowed to fall to a point slightly below the zero mark on the capillary tube *S*. The stopcocks *J* and *V* are then closed and the rubber tube at the bottom of the measuring burette is compressed by turning the screw *N* until the mercury stands exactly at the zero mark of the tube *S*. The stopcock *J* is then opened for a moment to bring the sample in the burette *A* to atmospheric pressure. The stopcocks *F* and *G* are next carefully opened to bring the air upon both sides of the manometer and in the compensating tube *C* to atmospheric pressure. In this operation care must be exercised to avoid driving out the drop of liquid from the tube *M*. *F* and *G* are now closed, the stopcock *K* is carefully opened, and the position of the drop of liquid in the manometer *M* is noted. The stopcock *K* is then closed, the stopcocks *V* and then *L* are opened, and the sample of air is driven over into the absorption pipette *B* where it is allowed to remain for one minute in contact with the absorbent. The level-bulb *E* is then lowered and the solution of potassium hydroxide in *B* is drawn up again to the mark, whereupon *L* is closed. The residual gas in the burette *A* is now brought approximately to atmospheric pressure by proper adjustment of the height of the level-bulb *E* and the stopcock *V* is then closed. *K* is opened and the drop of liquid in the manometer *M* is brought to its original position by turning the compression screw *N*. The final volume of the gas is now read off on the capillary tube *S* and the difference between this reading and the reading of the initial volume, expressed in divisions on this tube, corresponds to the parts of carbon dioxide per 10,000 in the sample of air under examination.

If the carbon dioxide in the sample is higher than 0.4 per cent, the wider graduated capillary tube *T* is employed in making the measurements, one division on this tube corresponding to one part of carbon dioxide per 1,000 parts of air.

A serious objection to the Pettersson-Palmqvist apparatus is its size and weight. It is also quite difficult to replace any of the glass parts that may be broken. Modifications of the apparatus, with a view to making it more easily portable, have been proposed by Bleier[28] and Rogers, but in the opinion of the authors, the objections to the original form are most satisfactorily met by the device described by Anderson[29] and shown in Fig. 97.

ANDERSON'S MODIFICATION OF THE PETTERSSON-PALMQVIST APPARATUS.—The gas is measured in the burette *A* and the change in volume of the sample that results when the carbon dioxide is absorbed is read upon the capillary *S*. This bent capillary tube passes through a stopper and is joined to the stopcock *V* by a piece of rubber tubing. This rubber tube passes under the compression screw *N* by means of which the fine adjustment of the mercury in the capillary tube *S* is effected. The other side of the stopcock *V* is connected with the level-bulb *E* by a piece of "varnished" rubber tubing. A solution of potassium hydroxide for the absorption of carbon dioxide is contained in the pipette *B*. *C* is the compensating tube, and

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[28] *Z. Hyg.*, **27**, 111 (1898).

[29] *J. Am. Chem. Soc.*, **35**, 162 (1913).

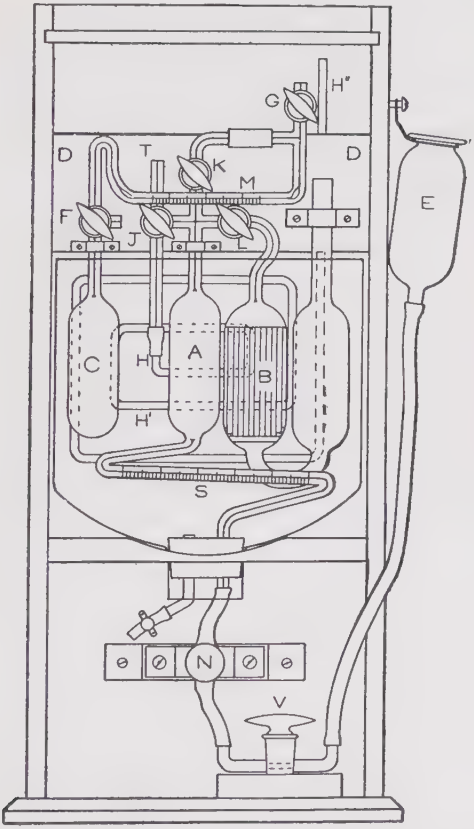

FIG. 97

M the manometer. By means of the three-way stopcock *J* the sample of air may be drawn through the coil of copper tubing, *H, H′ H″*. The compensating tube *C* may, by means of the three-way stopcock *F*, be brought into communication with the atmosphere through the side arm whenever necessary. The liquid index in the manometer is introduced through the stopcock *G*.

The burette, pipette, compensating tube, and the copper coil are immersed in water that is contained in a glass cell of rectangular cross section, and that is provided at the lower side with a neck like the neck of a bottle into which the rubber stopper shown in the figure is tightly inserted. In addition to the capillary tube *S* there passes through this rubber stopper a short piece of glass tubing through which the water in the cell may be run off. The glass parts of the apparatus in the cell are fastened to a sliding board *DD* above the cell. If the rubber stopper passing through the neck of the cell is loosened, and the rubber tube is slipped off from the lower end of *S*, the apparatus may be lifted from the case by raising the board to which it is attached. Ready access to all parts of the apparatus is thus easily attained, and the cleaning and repairing of the different portions is rendered easy. Furthermore, the position of the board may be adjusted, within certain limits, by means of the screw, a detail that is of importance in mounting new glass parts of slightly different dimensions from those of the former parts. The case is provided with a removable front and top and with a pane of glass at the back to illuminate the apparatus when it stands between the operator and the window.

This form of Pettersson-Palmqvist apparatus devised by Anderson is only 42 cm. high whereas the original apparatus has a height of 90 cm. Its small size and the ease with which it may be manipulated render it distinctly superior to the original design.

Before the apparatus is put into use the glass parts should, if necessary, be thoroughly cleaned, and the stopcocks should be carefully lubricated. In preparing the apparatus for use about 30 cc. of distilled mercury is poured into the level-bulb *E* and a small quantity of water is introduced into the burette through the opening *T* directly above the stopcock *J*. This is done by covering the end of this capillary tube with a film of water and drawing an amount of the liquid sufficient to form a column from 3 to 5 mm. long in the capillary tube into the burette by lowering the level-bulb.

The drop of liquid that is used in the manometer (petroleum in which azobenzene has been dissolved) is introduced into *M* by filling the burette *A* nearly to the top with mercury with the stopcocks *K* and *G* open, and then closing stopcock *V* and screwing down the compression screw *N*. A small amount of the manometer liquid is now brought upon the end of the capillary tube upon stopcock *G*, and an amount of the liquid sufficient to occupy a length of from 3 to 5 mm. in *M* is drawn into the capillary as far as the branch tube below stopcock *G* by turning back the compression screw *N*. Stopcock *G* is then closed, *F* is opened and the compression screw *N* is again turned down upon the rubber tube, and the liquid is, in this manner, forced into the manometer tube *M*.

The pipette *B* is filled with a solution of potassium hydroxide that is prepared by dissolving one part of potassium hydroxide in two parts of water. This solution is drawn up to the mark on the capillary by lowering the level-bulb *E*, and stopcock *L* is then closed.

Before proceeding with the determination of the carbon dioxide in the air of a room, the apparatus should be allowed to stand long enough in the room to insure equilibrium between the temperature of the water in the water jacket and the temperature of the air in the room. The air in the manometer tube *M* and in the compensating tube *C* should be brought to atmospheric pressure by opening the stopcocks *F* and *G*. During a determination the apparatus should not stand in direct sunlight or in a draft of air.

The actual determination of carbon dioxide is carried on as follows: Turn stopcock *J* to such position that the burette *A* communicates with the outer air through the tube *T*. Fill the burette *A* with mercury by opening stopcock *V* and raising the level-bulb *E*. Turn stopcock *J* to such position that the burette *A* communicates with the copper tube *H*, and draw air into *A* through *H* by lowering the level-bulb *E*. Inasmuch as this sample is mixed with air that was already present in the connecting tubes and the copper tube *H*, it is driven out through *T* by turning the stopcock *J* into the proper position and raising the level-bulb. Stopcock *J* is then turned back so that *A* communicates with *H*. The level-bulb E is again lowered and the sample of air is drawn into the burette *A* until the mercury in the burette falls slight below the zero mark on the capillary tube *S*. Stopcock *V* is then closed and the compression screw *N* is turned until the mercury stands exactly at the zero mark.

Allow stopcock *J* to remain open for a few moments to allow the air in the burette to assume atmospheric pressure and then close *J*. Open stopcock *K* carefully, and read the position of the liquid in the manometer *M*. Then close stopcock *K*. To remove the carbon dioxide in the sample, open stopcock *V* and then stopcock *L* and drive the gas over into the pipette *B*. When the mercury nearly reaches the stopcock *L*, close that stopcock and leave the gas in contact with the potassium hydroxide for one minute. Then lower the level-bulb, open stopcock *L*, draw the gas back into the burette, and when the solution of potassium hydroxide rises to the mark on the capillary close stopcock *L*. Bring the mercury approximately to the zero mark in the capillary *S* by raising or lowering level-bulb *E*, close the stopcock *V* and then turn the compression screw *N* until the mercury in the capillary tube *S* stands at such a point above the zero mark as will correspond approximately to the percentage of carbon dioxide in the air under examination. Then open stopcock *K* and turn *N* until the liquid in the manometer stands at the position that is occupied before the absorption was made. The reading of the mercury in the capillary tube *S* now gives directly the amount of carbon dioxide in the sample of air expressed in parts per 10,000.

HALDANE APPARATUS.—Another very satisfactory apparatus (Fig. 98) for the determination of small percentages of carbon dioxide is that proposed by Haldane.[30] He has also devised other forms [31] especially adapted to the examination of mine air, but only the first will here be considered.

The apparatus consists of a burette *A* which contains 20

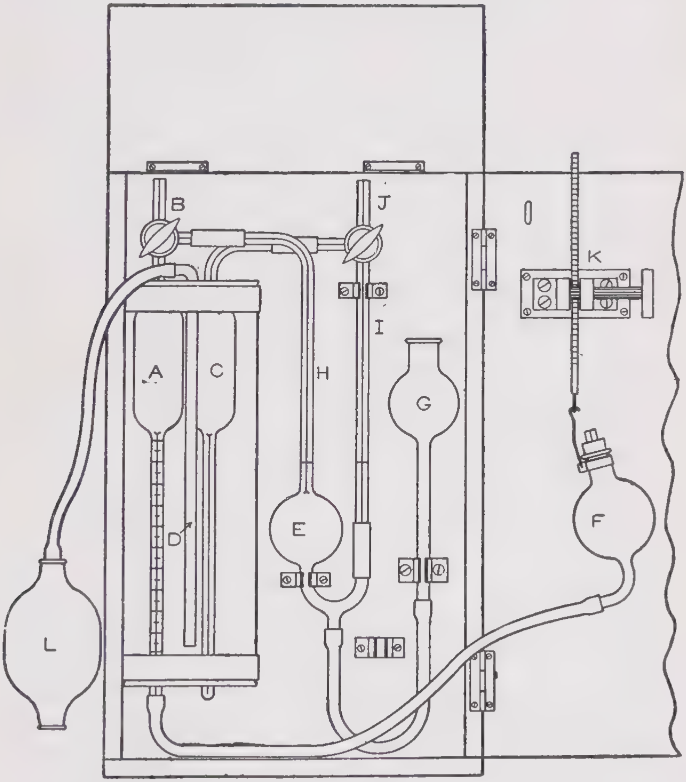

FIG. 98

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[30] *J. Hygiene,* **1**, 109 (1901); Haldane, *Methods of Air Analysis* (1918), p. 67; Frederick, *J. Soc. Chem. Ind.,* **35**, 96 (1916).

[31] *J. Physiology,* **22**, 466 (1898); Frederick, *Analyst,* **45**, 409 (1920).

cc. from the stopcock *B* to the zero point at the lower end of the capillary. The graduated part of the capillary is divided into about one hundred divisions, each of which corresponds to 0.0001 part of the total volume of the burette. The compensating tube *C* and the burette are surrounded by a water jacket, and each should contain a trace of dilute sulphuric acid to keep the air therein saturated with moisture. The water in the jacket may be mixed by blowing air through the glass tube *D* which extends to the bottom. One of the three-way connections of the stopcock *B* is used for introducing the sample of air, and a second connects the burette with the absorption pipette, *E*, containing a 10 per cent solution of potassium or sodium hydroxide.[32] *F* and *G* are the levelling bulbs for the burette and absorption pipette respectively. F is hooked into one of the holes in the rack-and-pinion device *K* by means of which accurate adjustment of the height of the mercury may be made.

In making a determination of carbon dioxide, the stopcock *B* is so turned as to connect the burette *A* with the absorption bulb *E* and the outside air, and by turning *J*, *I* is connected with the outside air and the compensating tube *C*. The level of the absorbent (a solution of caustic potash) is adjusted to the marks on tubes *H* and *I*, and the mercury in the burette to about the zero mark, by the rack-and-pinion device *K*. Stopcock *B* is now turned to connect the burette *A* with the outside air only, and the air is expelled from the burette by raising *F* in the hand. *F* is then replaced on the hook and mercury falls to the former mark near zero, thus drawing in the sample. *B* is then turned to connect the burette *A* with *E* only. Some mercury may be caught in the bore of *B*; this may be removed by now squeezing the rubber tube connecting the burette and *E* at the point nearest *B*. The mercury globule which drops into *A* can be united with the rest by closing *B* completely and gently raising *F*.

Stopcock *B* is again turned to connect *A* with *E* only, and stopcock *J* to connect *I* with *C* only. If the level of the absorbent in *I* has changed, it is brought back to the mark by raising or lowering *G,* and the level in tube *H* is brought to the mark by raising or lowering *F.* The rubber tubing connecting *G* and *E* should be squeezed to make certain that the potash solution moves freely in the two tubes and that the level of the potash solution returns to the marks. Air should be gently blown through the water jacket by squeezing the bulb *L,* while these adjustments are being made. When they are completed, the level of the mercury in the burette is read off on the graduated scale.

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[32] Frederick recommends coloring this solution with methyl orange to make the movement of the liquid more apparent.

The air is now passed over to the potash bulb and back four times, occasionally squeezing the bulb *L* to mix the water in the jacket. The mercury reservoir *F* is now replaced on the hook and, with a steady flow of air through *D,* the potash levels are adjusted to the marks on *H* and *I.* The mercury level in *A* is again read off, and the difference in the two readings gives directly the parts of carbon dioxide per 10,000. As soon as the test is completed, the stopcocks *B* and *J* should be turned to close communication in all directions since otherwise the potash solution may rise in the tubes and cause trouble.

Frederick [33] has devised a simple modification of the apparatus in which a graduated tube *H* is used, whereby a higher content than 100 parts per 10,000 may be determined. He also describes a device for lessening the labor of repeatedly raising and lowering the mercury level-bulb. A modified form for determining both carbon dioxide and oxygen in experiments on basal metabolism is given by Newcomer.[34]

McCoy and Tashiro [35] devised an apparatus (Fig. 99) for the determination of very small amounts of carbon dioxide.

A is a bulb of 25 cc. capacity, and all the capillary connecting tubes are one mm. bore except at *F* where it is widened to 2 mm. One side of *B* is connected to a reservoir of air free from carbon dioxide, and the other side to the burette containing the sample of air. One tube from *E* is joined to a bottle containing a perfectly clear 0.1 *N* solution of barium hydroxide, and the other tube is connected to a pump capable of reducing the pressure to 25 to 30 mm. of mercury. A level-bulb is attached to *D*.

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[33] *Loc. cit.*

[34] *J. Biol. Chem.,* **47**, 489 (1921).

[35] *Eighth Intern. Cong. App. Chem.,* **1**, 361 (1912).

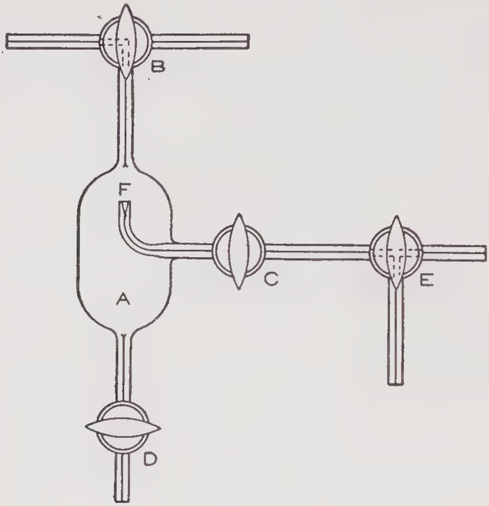

FIG. 99

Bulb *A* is cleaned and dried and is then evacuated through *C* and *E*. About 20 cc. of pure mercury is run into *A* through *D*, and the remaining 5 cc. is filled with air free from carbon dioxide. This air is then drawn out, the evacuation and rinsing being repeated four times. With 20 cc. of mercury in *A*, the clear solution of barium hydroxide is run through the capillary tube until a drop forms at *F*. The air sample is drawn into *A* in 0.5 cc. portions by withdrawing the mercury through D, and each successive portion is allowed to remain ten minutes to determine whether a visible precipitate of barium carbonate forms. The first visible precipitate indicates 1×10^{-7} grams of carbon dioxide.

Rosencrans[36] has devised an automatic gas analysis recorder for the determination of carbon dioxide in the air within the range of 0 to 3.5 per cent. This instrument utilizes the principle of the variation of thermal conductivity of the different gases (see Chap. XXI). Hill[37] says that this type of apparatus also serves admirably for the measurement of carbon dioxide in respired gas.

Weaver and Weibel[38] have described three new forms of instruments including the compensated bridge and glowing wire indicators, and the bimetallic detector, for the detection and automatic indication of the presence of combustible gases in the air.

[36] *J. Optical Soc. Am.*, **14**, 479 (1927).
[37] *J. Physiol.*, **56**, 20 (1922).
[38] *Bureau of Standards, Scientific Paper* No. 334 (1919).

CHAPTER XX

GAS-VOLUMETRIC ANALYSIS

NITROMETERS

Crum[1] observed that the higher oxides of nitrogen are completely reduced to nitric oxide when absorbed in sulphuric acid and then shaken with mercury. Watts[2] and Lunge[3] developed this method still further and the latter designed an apparatus for the evaluation of nitrates which he termed a nitrometer. For this specific purpose it is inferior to the nitrometer described on page 428, because the nitric oxide is evolved in the tube in which the gas volume is finally read, and the foaming of the acid renders difficult the accurate adjustment and reading of the height of the confining liquid. Usually an approximate correction is made for the pressure due to the acid layer by allowing one mm. of mercury for every 7 mm. of acid. Other methods have also been recommended[4] to overcome this difficulty.

A modified form of his nitrometer which Lunge later described[5] under the name of a ureometer, but which is generally known under the name of the Lunge nitrometer, is an instrument of wide application in gas-volumetric analysis.[6]

Lunge Nitrometer.—The instrument (Fig. 100) consists of a gas burette *A*, a level-tube *B*, and an evolution flask *C*. The burette has a capacity of more than 100 cc. It is provided at the upper end with a two-bore stopcock, and is graduated from the stopcock downward in 0.2 cc.

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[1] *Phil. Mag.*, **30**, 426 (1847).

[2] *Chem. News*, **37**, 45 (1878).

[3] *Ber.*, **11**, 434 (1878); **21**, 376 (1888); *J. Soc. Chem. Ind.*, **7**, 232 (1888); **11**, 778 (1892).

[4] Kaesbohrer, *Chem. Ztg.*, **42**, 296 (1918); Riviere and Pichard, *Bull. soc. chim.*, **35**, 901 (1924).

[5] *Ber.*, **18**, 2030 (1885); *J. Soc. Chem. Ind.*, **4**, 495 (1885).

[6] Lunge, *Chem. Ind.*, **8**, 161 (1885); *J. Soc. Chem. Ind.*, **9**, 21 (1890); Allen, *J. Soc. Chem. Ind.*, **4**, 178 (1885).

One of the two tubes of the stopcock is a short upright capillary tube of the usual diameter: the other tube is somewhat larger and is bent over until it points nearly downward. To it the evolution flask *C* is joined by a short piece of rubber tubing, the ends of the glass tubes being brought nearly together.

The evolution flask *C* usually has a capacity of about 100 cc. A short tube, open at the top, is fused to the bottom of the flask. A soft, one-hole rubber stopper carrying a short glass tube is inserted in the neck of *C*.

The nitrometer should be thoroughly rinsed with distilled water before a determination is begun, and the evolution flask should be carefully cleaned and dried. The apparatus should stand in a room of even temperature and should be protected from direct sunlight and drafts of air.

Manipulation of the Lunge Nitrometer.—In making a determination with the nitrometer, water or mercury is poured into the open end of the level-tube *B*, the stopcock *D* is opened, and the confining liquid is allowed to rise nearly to the stopcock which is then closed. The reacting substances are now placed in the evolution flask *C*, one in the outer space, the other in the tube. The short rubber tube carrying the stopper of *C* is slipped over the end of the bent tube of *D*, and the rubber stopper is then tightly inserted into the neck of the evolution flask. In doing this the neck of the evolution flask should be grasped between the thumb and fingers of one hand and the stopper be pushed into the neck of the flask with the other hand. The body of the flask itself should not be touched by the hand during the operation because this would warm the air in the flask and would cause error in the next adjustment. The air in *C* is slightly compressed by the insertion of the stopper. It is brought to atmospheric pressure by turning the stopcock *D* so that the evolution flask connects with the burette, and then bringing the confining liquid in the level-tube to the same height as that in the burette. The air in the evolution flask is now at atmospheric pressure. The stopcock D is turned through 180° while the tubes are in this position, and the level-tube is then raised until all of the air in the burette is driven out through the open capillary tube of the stopcock. The stopcock is turned to join *A* to *C*, and the substances in the evolution flask *C* are then brought together by taking hold of the rubber stopper of the flask and tipping it. The flask itself should not be touched with the hand. The reaction is allowed to proceed to completion, the flask being occasionally gently shaken. The gas that is set free passes over into the burette. The pressure thus caused is relieved from time to time by lowering the level-tube. When the evolution of gas has ceased, the confining liquid in the burette and level-tube is brought to the same height, and the volume of gas in the burette is read off.[7] The thermometer and barometer are read and the gas volume is corrected to standard conditions. The necessity for this correction may be avoided by using the Lunge gas volumeter (see p. 425) in place of the nitrometer.

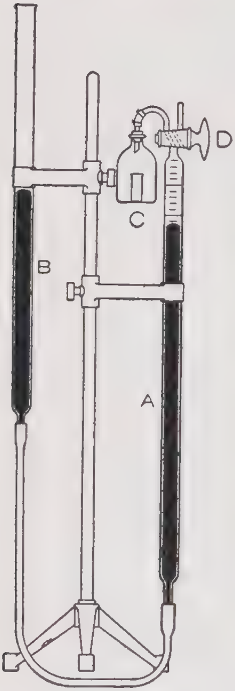

Fig. 100

This form of the Lunge nitrometer, or the Lunge gas volumeter, may be used for a variety of volumetric determinations such as the standardization of potassium permanganate, the analysis of hydrogen peroxide, bleaching powder or pyrolusite, and the determination of carbon dioxide in carbonates. For this last determination, however, the special forms of apparatus described by Chapin,[8] Shaw,[9] and Tubandt and Weisz[10] are probably more satisfactory.

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[7] If the heat of reaction of the substances in the evolution flask is appreciable, a beaker containing water of the temperature of the room should be brought up under the flask after the reaction is complete and the flask should be allowed to stand immersed in the water for a period of five minutes before the volume of gas in the burette is measured.

Lunge Gas Volumeter.—To facilitate work with the nitrometer, Lunge[11] devised an instrument, the gas volumeter, with the aid of which a volume of gas in the measuring tube of the apparatus may quickly be brought to the volume that it would occupy under standard conditions. This does away with the usual calculations and effects a considerable saving of time.

The instrument, Fig. 101, consists of a gas burette, *A*, a reduction tube *B*, and a level-tube *C*, which are connected at the lower ends by pieces of "varnished"[12] rubber tubing, and the T-tube *D*.

The gas burette *A* has a capacity of somewhat more than 100 cc. and is graduated from the stopcock downward in 100 cc. divided into 0.2 cc. At its upper end is a two-way stopcock *S*. The upper tubes of the stopcock are capillary and one of them is bent over and downward as shown in the figure.

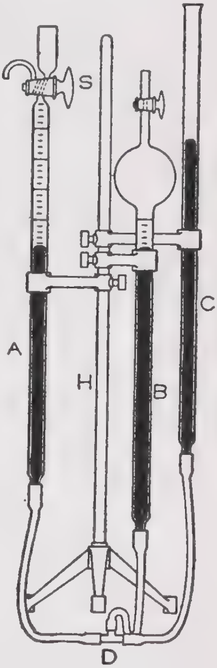

FIG. 101

The reduction tube *B* is provided with a single bore stopcock at the upper end. Below the stopcock it is widened into a bulb. From the stopcock to a mark on the tube somewhat below the bulb the tube holds exactly 100 cc. From the 100 cc. mark downward the tube is graduated to about 140 cc. in 0.1 cc.

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[8] *Ind. Eng. Chem.*, **10**, 527 (1918).

[9] *Ind. Eng. Chem.*, **13**, 1151 (1921).

[10] *Chem. Ztg.*, **46**, 1105 (1922).

[11] *Ber.*, **23**, 440 (1890); **25**, 3157 (1892); *Z. angew. Chem.*, **3**, 139 (1890); **4**, 197, 410 (1891); **5**, 677 (1892); *J. Soc. Chem. Ind.*, **9**, 547 (1890).

[12] See p. 100.

The level-tube *C* is a plain tube open at the top. The three tubes are fastened in clamps that are attached to the iron stand *H*.

To prepare the apparatus for use it is first necessary to inclose in the reduction tube a volume of moist air that, under standard conditions and in the dry state, would have a volume of exactly 100 cc. This is accomplished as follows:

The apparatus is filled with clean mercury and somewhat more than 100 cc. of air is then drawn into the reduction tube *B* by opening the stopcock of the tube and lowering the level-tube *C*. A drop of water is next drawn into the bulb of *B* through the stopcock to insure that the space above the mercury in the reduction tube is saturated with water vapor. A thermometer is hung close to the apparatus, and after the apparatus has come to the temperature of the room, the thermometer and barometer are carefully read.

The volume that 100 cc. of air, under standard conditions, would occupy under the observed temperature and pressure is now calculated from the formula,

$$\mathrm{v} = \mathrm{v}_0 \frac{760(1 + .00367\,\mathrm{t})}{\mathrm{p} - \mathrm{m}}$$

which is derived directly from (8) on p. 32, and in which $\mathrm{v}_0 = 100$ cc.

The stopcock of the reduction tube is now opened, and the level-tube is raised or lowered until the mercury in *B* stands exactly at the volume calculated for v. The stopcock of *B* is then closed. There is thus inclosed in the reduction tube a volume of air that will occupy exactly 100 cc. when measured under standard conditions.

If now a gas is brought into the burette *A*, the volume that it would occupy under standard conditions may rapidly be ascertained in the following manner.

The level-tube *C* is raised or lowered until the mercury in the reduction tube *B* stands close to the 100 cc. mark, and *C* is then clamped firmly in that position. The burette *A* is now raised or lowered until the mercury in it stands at the same height as that in the reduction tube and it is then clamped in position. This adjustment will usually cause the mercury to move up or down from the 100 cc. mark in *B*. It is brought back to the mark by again changing the height of the level-tube, and the burette is again raised or lowered until the mercury in it and in *B* are at the same level. These adjustments are repeated until, with the mercury in *A* and *B* at the same height, the mercury in the reduction tube *B* stands exactly at the 100 cc. mark.

Since the pressure upon the air in *B* suffices to bring it, at the now prevailing temperature, to the volume that it would occupy under standard conditions, it follows that the gas in the burette *A*,[13] if at the same temperature as the air in *B*, will also be brought to the volume that it would occupy under standard conditions, and consequently its corrected volume may be directly read off.

The Lunge gas volumeter is open to criticism because the burette and the reduction tube stand free in the air and for that reason are subject to sudden and different changes of temperature. This may cause appreciable error since a difference of only 1° C. would mean a variation of 0.3 per cent in the gas volume. For this reason the apparatus will give dependable results only when it stands in a room of uniform temperature and free from drafts, and when in the manipulation great care is exercised to avoid the uneven warming of the tubes by heat from the hands or from the body of the operator.

Japp[14] has modified this apparatus so that, with an ordinary graduation in cubic centimeters, any single gas may be measured under such conditions that each cubic centimeter represents a milligram of the gas. Deming[15] has also suggested a modification whereby the gas volume is not only reduced to standard conditions but is also converted automatically into the percentage of any desired constituent, no matter what the nature of the substance analyzed, for any weight of sample.

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[13] The space above the mercury in *A* must of course be saturated with water vapor as is the space in *B*.

[14] *J. Chem. Soc.*, **59**, 894 (1891).

An ingenious instrument with the aid of which the weight of the gas in the measuring burette may be calculated in a very simple manner from its pressure is that devised by Bodländer.[16] It may also be used as a mercury pump in the same manner as the Hempel burette (see p. 11).

Nitrometer.—The reaction studied by Crum[17] has been utilized by Hempel[18] in the determination of the nitroglycerine in dynamite. For this work he designed a special nitrometer which is also admirably adapted to the evaluation of saltpeter. In its original form, however, the Hempel nitrometer is open to objection because the rubber stopper that carries the sample tube is kept in place only with difficulty, and further because of the awkwardness of cleaning the apparatus after a determination has been made. Dennis has sought to remedy these defects by giving to the nitrometer the form shown in Fig. 102.

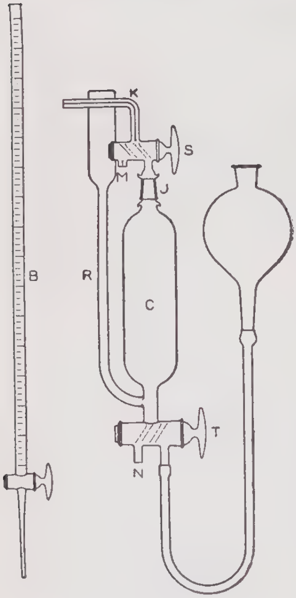

Fig. 102

The evolution cylinder C is provided at the lower end with the double-bore stopcock T and the side arm R. The stopcock *S*, also of double bore, is attached to the upper end of the cylinder by the carefully ground joint *J* and is held in place by rubber bands or steel springs slipped over the small glass hooks above and below the joint. *K* is a capillary tube which serves to connect the nitrometer with the gas burette in which the evolved nitric oxide is measured. *A* level-bulb is joined to one arm of the stopcock *T* by a piece of "varnished" rubber tubing.

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[15] *J. Am. Chem. Soc.*, **39**, 2145 (1917).

[16] *Z. angew. Chem.*, p. 425 (1894). See also Dennis, *Gas Analysis* (1913), p. 40.

[17] Crum, *loc. cit.*

[18] *Z. anal. Chem.*, **20**, 82 (1882).

The manipulation of the apparatus in the evaluation of saltpeter or other nitrate is as follows: Place the evolution cylinder *C* in a large clamp and attach it to an iron stand in an upright position. Place the level-bulb in a split ring that is also attached to the rod of the iron stand and introduce into it an amount of mercury sufficient to fill the evolution cylinder *C*, the side arm *R*, and the rubber tube. Remove the stopcock *S* from the top of the cylinder *C*, turn the stopcock *T* into such position that the level-bulb and *C* will be in communication, and fill the evolution cylinder *C* with mercury to a point about 5 cm. below the top of the tube *J*. Introduce into the upper end of *C* through the open tube *J* about 5 cc. of a solution of the nitrate to be analyzed, running in the solution from the small burette *B*, which is calibrated in tenths of a cubic centimeter and can easily be read to fiftieths. Place the stopcock *S* upon *J* and fasten it in position by rubber bands or steel springs attached to the small hooks on either side of the joint. Raise the level-bulb until the top of the solution in *C* just reaches the lower side of the stopcock *S* and then close *S* and *T*. Lower the level-bulb and then carefully open the stopcock *T* until the mercury in the side arm *R* falls to about the beginning of the bend in that tube.

Introduce a measured amount (about 20 cc.) of concentrated sulphuric acid into the upper open end of *R*. Remove *C* from the clamp and hold it in an inclined position, with the tube *R* on the upper side, at such height that the mercury in *R* stands at the same level as that in the level-bulb. Turn the stopcock *T* to such position that the level-bulb communicates with *C* and then slowly raise *C* (still holding it in an inclined position) until all but about 5 cc. of the sulphuric acid has been drawn into the evolution cylinder *C*. Now lower *C* until the mercury rises to about the middle of the tube *R* and then close the stopcock *T*. Shake[19] the cylinder *C* to insure intimate mixing of the sulphuric acid with the solution of the nitrate. As the reaction proceeds the evolution of gas tends to force the mercury upwards in the side arm *R*. The level of the mercury in this arm is kept approximately the same during the reaction by opening the stopcock *T* from time to time and allowing the mercury to flow back into the level-bulb. The shaking of the evolution cylinder *C* is continued until, with the stopcock *T* closed, no further rise of the mercury in *R* is observed. The reaction is then complete.

C is now again clamped in a vertical position and the capillary tube *K* is attached by means of a small **L**-shaped piece of capillary tubing to a Hempel gas burette that contains mercury as the confining liquid and into which a very little water has been introduced. The stopcock *S* is then turned to such position as to connect *K* with the outlet *M*, and the level-tube of the burette is raised until the capillary tube *K* is completely filled with mercury. *S* is now turned through 180° so that the cylinder *C* communicates with the tube *K*. *T* is then turned to such position that the level-bulb and *C* are connected, and the evolved gas is drawn over into the burette, the sulphuric acid in the nitrometer being allowed to follow the gas until it almost reaches the end of the capillary tube *K*. The stopcock *S* is then closed, the pinchcock at the top of the burette is also closed and the nitric oxide in the burette is measured in the usual manner, due allowance being made for the tension of water vapor.

After a determination has been made, the nitrometer is cleaned by lowering the level-bulb, opening the stopcocks *S* and T and allowing the *clean* mercury to flow back into the level-bulb. The stopcock T is then turned into the position shown in the figure and the dirty mercury, mercurous sulphate, and sulphuric acid are allowed to run out through the tube N into a beaker. The stopcock S is next slipped off from the upper end of the cylinder C and the side arm R as well as the wide tube of the stopcock S are thoroughly rinsed with water and are then dried.

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[19] Marqueyrol and Florentin, *Bull. soc. chim.*, **9**, 231 (1911), have found that prolonged shaking may cause the reduction of nitric oxide to nitrous oxide and nitrogen.

In calculating the results of the analysis allowance must be made for the solubility of nitric oxide in sulphuric acid. Webb and Taylor[20] found that Lunge's[21] value for this solubility is too high for 91 to 92 per cent acid. They state that 10 cc. of the acid dissolves 0.2 cc. of nitric oxide, which agrees with the results of Tower.[22] Joyce and La Tourette[23] ascertained that the solubility of nitric oxide decreases markedly above 28°.

The purity of the nitric oxide that is evolved may be ascertained by passing the gas, after it has been measured in the burette, into a double gas pipette for liquid reagents that contains in the first two bulbs a solution of a ferrous salt, and in the last two, water.

It has been found that the nitrometer method is not satisfactory for the determination of nitrogen in carbon ring compounds,[24] and that the presence of over 15 to 17 per cent sodium chloride[25] on a dry basis or of iron[26] in any form renders the results unreliable.

In the evaluation of saltpeter the sample should be dissolved in a little water and 5 cc. of this solution is used in the analysis. The concentration of this solution should be such that about 75 cc. of nitric oxide will be evolved.

In the analysis of solid material a weighed sample of the substance is introduced into the upper open end of the evolution cylinder *C*. The sample is moistened with a little water, the stopcock *S* is then placed in position and fastened with rubber bands or steel springs, mercury is driven up to the lower side of the stopcock *S*, and the further analysis is then carried out in the manner above described.

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[20] *J. Soc. Chem. Ind.,* **41**, 362 (1922).
[21] *Ibid.,* **4**, 447 (1885).
[22] *Z. anorg. Chem.,* **50**, 382 (1906).
[23] *Ind. Eng. Chem.,* **5**, 1017 (1913).
[24] Joyce and La Tourette, *loc. cit.*
[25] Sanders, *Ind. Eng. Chem.,* **12**, 169 (1920).
[26] Jones, *ibid.,* **17**, 144 (1925).

In the analysis of gun-cotton Hagen first shakes the sample with concentrated sulphuric acid in the evolution cylinder *C* for three minutes, and then when the gun-cotton is dissolved, he heats *C* by holding it in an inclined position over a Bunsen burner, and continues the shaking of *C* as long as evolution of gas is observed.

Du Pont Nitrometer.—An instrument very extensively used in this country for the determination of nitrogen in either organic or inorganic nitrates is the du Pont nitrometer.[27]

The evolution bulb *A* of this nitrometer (Fig. 103), has a capacity of about 300 cc., and is provided at the lower end with a stopcock and a rubber tube connecting with the reservoir *B*. The double-bore stopcock at the top carries a cup *E*, and a capillary tube to which either burette *C* or *D* may be attached. Senften[28] suggests that this evolution cylinder should be made with a ground joint as shown in Fig. 102. *F* is another reservoir which is connected by rubber tubing and the glass multiple connecting-tube *G*, with the compensating burette *H* and the measuring burettes *C* and *D*. The measuring and compensating burettes *C* and *H* are of the same size and shape and have bulbs at the top. *H* is not graduated. The measuring burette *C* is so graduated that the percentages of nitrogen may be read directly therefrom, and is marked to read from 10 to 14 per cent in one-hundredths of one per cent. The 10 per cent mark represents a volume of 171.8 cc. of nitric oxide at 20° C. and 760 mm. pressure which contains 0.1 gram of nitrogen. The 14 per cent mark is equal to 240.4 cc. of nitric oxide under the same conditions, and contains 0.14 gram of nitrogen.

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[27] Pitman, *J. Soc. Chem. Ind.*, **19**, 982 (1900); Lunge, *ibid.*, **20**, 100 (1901); Snelling and Storm, *Bureau of Mines, Bulletin* No. 51 (1913); Cope and Taylor, *Bureau of Mines, Tech. Paper* No. 160 (1917).

[28] *Chem. Ztg.*, **40**, 39 (1916).

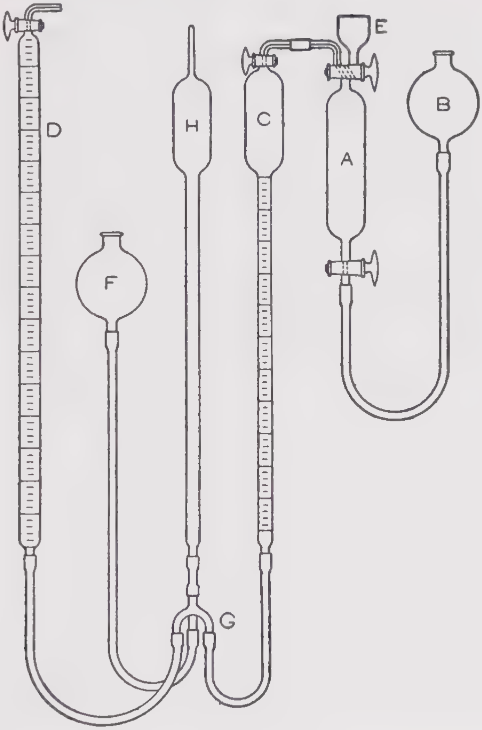

FIG. 103

The other measuring burette *D* is graduated to read from 0 to 100 per cent in tenths of a per cent. The burette is of such a size that 0.30 gram of nitric oxide at 20° C. and 760 mm. pressure will fill it to the 100 mark. The percentages of nitrogen may be read directly in this burette if a 0.14 gram sample of the substance is used. If $\frac{1}{100}$ of a gram molecule of the substance is taken, the readings give directly the percentage purity of the original substance. This is convenient when it is not certain that the liberated nitric oxide will fill the burette *C* between the 10 and 14 marks.

All of the tubes are supported with holders which may be moved up and down on the vertical support rods, and are so arranged that the weight of the tube presses them down and acts as a brake which prevents their changing position when not being manipulated. The support for the evolution bulb *A* is so designed that the cylinder may be removed by raising it slightly and bringing it forward, thus avoiding any manipulation of a screw as with an ordinary clamp.

Standardization.—Before the nitrometer may be used for making a determination, it must be standardized. After setting up the apparatus and filling it with mercury, it may be standardized by either of the following methods, although the second method is preferable.

Dry Air.—About 20 to 30 cc. of sulphuric acid and 210 cc. of air are drawn into the evolution bulb *A* through *E*, the stopcocks are closed, and the bulb is thoroughly shaken to dry the air. The dry air is then run into the compensating burette *H* until the mercury stands at about the 12.5 per cent mark in the measuring burette *C* with the two tubes at the same height. The top of the compensating burette is then sealed off. A second portion of air is dried in the same manner and is run into the measuring burette *C* until the mercury is at about the 12.5 per cent mark. The stopcock is then closed, and a small U-tube filled with sulphuric acid is attached to the outlet of the burette *C*. After the air in the burette has come to room temperature, the mercury columns in *C* and *H* are adjusted to about the same height, the burette stopcock is carefully opened, and the sulphuric acid is brought to the same height in both arms of the U-tube, the mercury in *C* and *H* being also adjusted to exactly the same level. The burette is now read, noting at the same time the barometric pressure and the room temperature.

Using the formula (see Chap. III),

$$V_0 = V\frac{p(273 + t)}{760(273 + t')}$$

or, more accurately, taking into account the expansion of mercury, when

$$V_0 = V\frac{p(273 + t)(1 - 0.00018\,t')}{760(273 + t')(1 - 0.00018\,t)}$$

the volume that the enclosed air would occupy at 760 mm. pressure and at a temperature t, 20° C., is calculated. The stopcock is now closed and the reservoir *F* and tubes are so adjusted as to bring the air in *C* to the calculated volume, with the mercury in *H* at the same level as in *C*. The height of the mercury in the compensating tube is now marked on the tube.

Potassium Nitrate.—A shorter and preferable method of standardization is with chemically pure potassium nitrate. In this method the compensating burette *H* is filled with dry air as described above. One gram of pure potassium nitrate, dissolved in 2 to 4 cc. of water, is introduced into the evolution bulb through *E*, and the cup is washed with a total of 20 cc. of sulphuric acid in three or four separate portions, each portion being run separately into the bulb. The leveling-bulb *B* is lowered, and the bulb *A* is gently shaken until the nitric oxide begins to be evolved. When all but about 60 cc. of mercury has run out of *A*, the lower stopcock is closed and the bulb is shaken vigorously for from three to five minutes. The bulb is then replaced in the holder and the nitric oxide is run over into the measuring burette *C*. The theoretical percentage of nitrogen in potassium nitrate is 13.86. With the stopcock closed, the mercury level is adjusted so that it stands at 13.86 in the burette, with the mercury in *H* at the same level. The height of the mercury in the compensating tube is now marked on the tube.

This method has the advantage that no readings of temperature and pressure are necessary, and it also compensates for any error due to impurities in the sulphuric acid. If a new supply of sulphuric acid is used, the nitrometer should be restandardized.

The actual determination is made exactly as in the standardization with potassium nitrate, using a sample that is not too large or too small to fall within the graduations on the burette. Nitro compounds[29] which may be nitrated further, and oils and greases, etc., give low results with a nitrometer. In such cases, the nitrate should be separated from the interfering substances with a suitable solvent.[30]

Azotometer.—The determination of ammonia in its salts may be made by their decomposition with sodium hypobromite and measurement of the liberated nitrogen in an instrument known as an azotometer.[31] It consists essentially of an evolution bottle connected to a burette and levelling tube enclosed in a water jacket. The reaction is

$$2\,NH_3 + 3\,NaOBr = N_2 + 3\,NaBr + 3\,H_2O.$$

The method gives results of only approximate accuracy because the decomposition of the ammonium salt is usually incomplete. It has been suggested that 2.5 per cent be added to the volume of the liberated nitrogen to compensate this error.

[29] Storm, *Bureau of Mines, Bulletin* No. 96 (1916).

[30] Storm, *loc. cit.;* Hyde, *J. Am. Chem. Soc.*, **35**, 1173 (1913).

[31] Knop, *Chem. Zentr.*, **5**, 244 (1860); *Z. anal. Chem.*, **14**, 247 (1874); Wagner, *Z. anal. Chem.*, **9**, 225 (1870); **13**, 383 (1874); **15**, 250 (1876); Lunge, *Chem. Ind.*, **5**, 165 (1885).

CHAPTER XXI

PHYSICAL METHODS OF GAS ANALYSIS

Within recent years great advances have been made in devising methods of gas analysis which are based upon the physical characteristics of gases, such as refractivity, thermal-conductivity, vapor pressure, and diffusion.

REFRACTIVITY

The determination of the refractivity of gases probably originated with Dulong.[1] Rayleigh [2] devised a simple apparatus for this determination and described the essential features of the method, but no application was made until the development of the Rayleigh-Zeiss interferometer by Haber and Löwe.[3]

For any particular wave-length of light, the refractivity of a gas may be regarded as the increased retardation of the velocity which occurs when light of that wave-length passes through a layer of the gas. Thus if the time of passage of light through a vacuum is unity, and n is the time of passage through the same space filled with the gas, which is the refractive index of the gas, then the refractivity is equal to the difference, or

$$R = n - 1$$

The refractivity of a gas is proportional to its density,[4] or

$$\frac{R}{d} = \text{a constant,}$$

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[1] *Ann. chim. phys.*, **31**, 154 (1826).

[2] *Proc. Roy. Soc.*, **59**, 201 (1896).

[3] *Z. angew. Chem.*, **23**, 1393 (1910); Stuckert, *Z. Elektrochem.*, **16**, 37 (1910); Burrell and Siebert, *Bureau of Mines, Bulletin* No. 42 (1913); Adams, *J. Am. Chem. Soc.*, **37**, 1181 (1915); Siebert and Harpster, *Bureau of Mines, Tech. Paper* No. 185 (1918); Löwe, *Chem. Ztg.*, **45**, 405 (1921).

[4] Gale, *Phys. Rev.*, **14**, 1 (1902); Matthews, *J. Frank. Inst.*, **117**, 673 (1914).

and since the density of a gas is proportional to its pressure, it follows that the refractivity of a gas will follow the gas laws insofar as the gas itself obeys the same laws. Thus, if R_0 is the refractivity of a gas at 0° and 760° mm., the refractivity at any other temperature t and pressure p will be

$$R = R_0 \frac{273}{273 + t} \cdot \frac{p}{760}.$$

Furthermore, in a mixture of gases, the total refractivity will be equal to the sum of the products of the refractivity of each gas at standard pressure multiplied by its partial pressure,[5]

$$R = R_1 \frac{p_1}{p} + R_2 \frac{p_2}{p} + \text{etc.}$$

or, in the case of a binary mixture containing X per cent of one component,

$$R = R_1 \frac{100 - X}{100} + R_2 \frac{X}{100}.$$

The gas interferometer does not measure directly the absolute refractivity of a gas, but gives rather the difference of refractivity of two gases. If the foregoing gas mixture were compared with a single gas of refractivity R_1, the difference in refractivity $\triangle R$ indicated by the interferometer would be

$$\Delta R = R_1 - R = R_1 - \frac{R_1(100 - X) + R_2X}{100}$$

$$\Delta R = \frac{(R_1 - R_2)X}{100}.$$

If R_1 and R_2 are the refractivities at 0° and 760 mm., and the measurements are made at a temperature t and pressure p, the relation becomes

$$\Delta R = \frac{273}{273 + t} \cdot \frac{p}{760} \cdot \frac{(R_1 - R_2)X}{100} \qquad (1)$$

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[5] Valentiner and Zimmer, *J. Chem. Soc.*, **106**, 81 (1914); Edwards, *Bureau of Standards, Tech. Paper* No. 131 (1919); *Chem. Met. Eng.*, **21**, 560 (1919).

The interferometric method is satisfactory only for binary gas mixtures or their equivalent. The general procedure is to use as the gas of comparison the same gas mixture as the one to be tested, except that the constituent to be determined has been removed. This renders this method of much wider use than if only pure gases or air were employed as standards of comparison.

Interferometer.—There are two models of the Rayleigh-Zeiss interferometer in general use, the small portable type,[6] and the larger and more accurate laboratory model. A diagrammatic sketch of the laboratory type of interferometer is shown in Fig. 104.

The rays of light from the lamp *A* are made parallel by the object glass of the collimeter *B* and are then divided into two beams by the vertical rectangular openings r_1 and r_2. The upper halves of these beams of light pass through the air to the plate *C*, which deflects the light downward to blot out from the field the dark band caused by the thickness of the metal tubes *D* and *E* that confine the gases. The two beams of light are united at the eyepiece *I* by the lens of the observation telescope *F*, and an image of the slit is produced with Fraunhofer diffraction bands which appear as two parallel dark bands in the white field, with colored bands on both sides. Since the beams of light have equal optical paths, these bands have a fixed position and are used as the reference points.

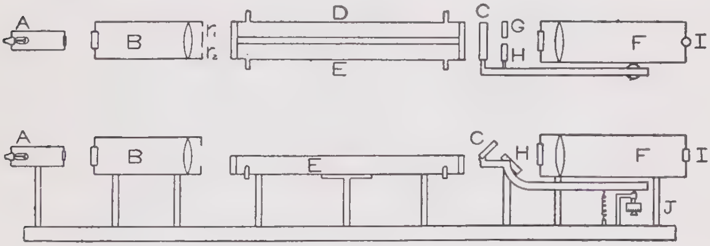

Fig. 104

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[6] Pouchon, *Chimie et industrie,* **2,** 647 (1919); *Chem. Met. Eng.,* **21,** 392 (1919).

The production of these interference bands may be explained from Fig. 105. Light from the source *A* passes through the two slits r_1 and r_2 and the two beams overlap as they fall on the screen *I*. At the point *O*, equidistant from r_1 and r_2, they will arrive in the same phase, and a luminous band results. However, at point *P* the paths of the two beams are of different lengths. If r_1P differs from r_2P by a half wave-length or any odd number of half wave-lengths, then the waves of light arrive in the opposite phases and a dark band results. If, however, r_1P differs from r_2P by a whole wave-length or any number of complete wave-lengths, then they will arrive in the same phase and a bright band appears. In this way there is formed on the screen a series of alternate bright and dark bands. With monochromatic light the bands are alternately black and of the color of the source of light, but with white light only, the center band is white and the others are rainbow-colored, with the inner edges of the bands violet and the outer edges red. The diffusion is greater the farther the band is away from the center.

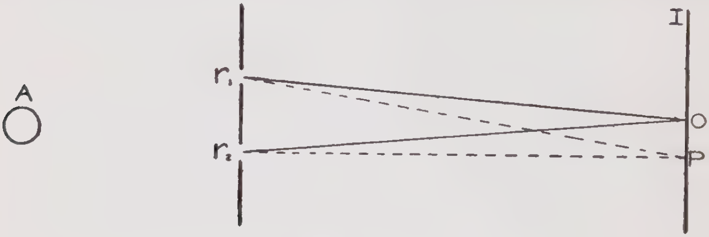

FIG. 105

The lower halves of the beams of light (Fig. 104), pass through the two separate gas chambers *D* and *E* which are about 100 cm. long and closed at the ends with plane-parallel glass plates. Each chamber has an inlet and an outlet tube for filling it with gas. The beams of light then pass through the compensator plates *G* and *H* and are brought together at *I* to form the lower half of the field. If the composition of the gases in the two tubes is different, the optical paths will be different, and the interference bands at *I* will be displaced from their normal position. The compensator plate *H* can be tilted by the micrometer screw *J*, which allows for adjustment of the optical path through *E*. The angle through which the compensator plate *H* must be turned to bring the two optical paths to equality, as shown by the coincidence of the interference bands in the upper and lower halves of the field, is a measure of the difference between the refractivity of the gases in *D* and *E*. The adjustment necessary is read from the micrometer screw *J* which acts on a lever arm attached to *H*.

The accuracy of the interferometer, all other factors being equal, will depend upon the length of the gas chambers, and an instrument of the above type will give results accurate to within 0.02 to 0.03 per cent. This is equivalent to that of ordinary volumetric apparatus using mercury as the confining liquid. The gases in the two chambers must be dry and must have the same temperature [7] and pressure, because a change in the temperature and pressure as well as in the composition will make the optical paths different. The temperature at which the determination is made should be the same as that of the calibration, for a change of 3° will introduce an error of about one per cent. The pressure in the two chambers is often equalized by fitting the outlet tubes with capillary tubes, but it can more accurately be determined by a water gauge, with a drying tube inserted between the gauge and the chamber to prevent diffusion of water vapor into the chamber.

The accuracy of the determination will also depend upon the difference of refractivity of the different gases. These should differ by about 0.0001 to insure the above-mentioned accuracy.

The refractivities of the common gases for the sodium line, which represents the average wave-length of light used in interferometer, are given in Table XIX.

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[7] Pouchon, *loc. cit.*

TABLE XIX[8]

Refractivity of Gases

(0° C. and 760 mm.)

Gas	Formula	Refractivity ×10⁻⁷	Ideal Refractivity ×10⁻⁷
Air		2917	2916
Acetylene	C_2H_2	6020	5971
Ammonia	NH_3	3820	3778
Argon	A	2809	2807
Carbon monoxide	CO	3347	3346
Carbon dioxide	CO_2	4498	4467
Cyanogen	C_2N_2	8490	8320
Ethane	C_2H_6	7660	7578
Ethylene	C_2H_4	7266	7209
Helium	He	0342	0342
Hydrogen	H_2	1387	1388
Krypton	Kr	4270	4259
Methane	CH_4	4415	4408
Neon	Ne	0671	0671
Nitric oxide	NO	2950	2947
Nitrogen	N_2	2972	2971
Nitrous oxide	N_2O	5160	5122
Oxygen	O_2	2706	2704
Sulphur dioxide	SO_2	6760	6628
Xenon	Xe	7020	6968

Calibration of the Interferometer.—The usual method of calibration is to place a standard gas in one chamber, and to determine the shift of the interference bands when known percentages of the constituent to be determind are added to the standard gas in the other chamber.[9] In this method, however, the results will not be correct if the mixture of gases varies from an accurately known composition. To meet this difficulty, Edwards[10] has devised a method of calibration in which both chambers are filled with dry air, free from carbon dioxide, at a definite temperature and pressure. The pressure in one chamber is then progressively varied, noting the reading of the micrometer screw necessary to give coincidence of interference bands for each pressure. The difference in refractivity for each scale reading can be calculated from the formula

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[8] *Bureau of Standards, Tech. Paper* No. 131 (1919).

[9] Siebert and Harpster, *loc. cit.*; Wolff, *Chem. Ztg.*, **38**, 347 (1914).

[10] *J. Am. Chem. Soc.*, **39**, 2382 (1917); *Bureau of Standards, Scientific Paper* No. 316 (1917); Werner, *Z. angew. Chem.*, **38**, 905 (1925).

$$\Delta R = \frac{273 \times 0.0002917(p_1 - p_2)}{760\ T} \qquad (2)$$

in which p_1 and p_2 are the pressures in the two chambers, and T is the absolute temperature which remains constant. 0.0002917 is the refractivity of air at 0° and 760 mm. pressure.

From the curve of refractive differences, determined as above, plotted against scale readings, the scale readings that correspond to the refractive differences of any gas for which the calibration is desired can be calculated from equation (1) on page 438. The results may then be plotted on a curve showing the percentage of the desired constituent for any scale reading. It is convenient to construct calibration curves for different intervals of temperature and pressure so that correct readings may be obtained by interpolation.

In case the gas deviates appreciably from the simple gas laws, this deviation should be taken into account because the refractivity at low partial pressures may differ from the value calculated from the ratio of the pressures.[11] For these calculations the values for the "ideal refractivity"[12] of the gas, given in Table XIX, should be used. These are the values calculated from the refractivity at very low pressures.

Operation.—The zero point of the instrument should first be established by filling both chambers with dry air, free from carbon dioxide and at the same temperature and pressure, and noting the position of the micrometer screw. This may be taken as the zero point, or the micrometer screw may be set at zero and the plate *G* moved to the position where the interference bands in the two halves of the field coincide. The lens in front of the lamp *A* should be so adjusted that the slit in the collimator tube is in its focus, otherwise there may be different intensities of the bands in the center of the field. The determination is made as previously described, the gases being dry and being maintained at some definite temperature and pressure. In case it is desired to examine gases in a closed system, a pump[13] may be inserted to automatically circulate the gases.

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[11] Edwards, *loc. cit.*

[12] Jones and Partington, *Phil. Mag.*, **29**, 28 (1915).

Applications.—Among the numerous uses of the interferometer, the following will serve to illustrate its application. It has been used to determine carbon dioxide in air and in flue gases,[14] the purity of many gases, the benzol content of illuminating gas, sulphur dioxide in gases in connection with the manufacture of sulphuric acid, the ammonia content[15] of gases in the synthetic manufacture of ammonia, methane in mine air, the purity of helium from the fractional liquefaction of natural gas, and the study of the reversible reactions of carbon monoxide on the oxides of iron.[16]

THERMAL-CONDUCTIVITY

The analysis of gases by the thermal-conductivity method was suggested by Somzie about 1880. The temperature of a wire, stretched along the axis of a glass tube that is immersed in a water bath, and heated by an electrical current of constant strength, will vary with the nature of the gas that surrounds the wire. Schleiermacher[17] utilized this principle in determining the thermal conductivity of gases. Koepsel[18] developed an instrument based on this principle for the determination of hydrogen in producer gas and proposed its use for the determination of carbon dioxide in flue gas and of methane in mine gases. Goldschmidt[19] improved Schleiermacher's method by using two wires of different lengths enclosed in silver capillary tubes inserted in a brass block. This method was also employed by Eucken[20] in measuring the thermal conductivities of gases. However, in spite of the accuracy and simplicity of this method, it remained practically unknown until much later. The Siemens and Halske Company improved Koepsel's procedure by passing the gases through the same metal block to bring them to identical temperatures. They later described[21] the application of the method to the determination of carbon dioxide in flue gas. Shakespear[22] developed a practicable and accurate instrument for the determination of the purity of the gas used in filling balloons, which he calls a "Katharometer." Later the Bureau of Standards[23] made a thorough investigation to determine the most practical form of apparatus and the application of the method to various industrial processes.

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[13] Skossarewski and Germann, *J. chim. phys.*, **11**, 584 (1913); Menzies, Collins and Tyson, *Science*, **61**, 288 (1925); Pearson and Thomas, *J. Chem. Soc.*, **127**, 2450 (1925); Chatterji and Finch, *ibid.*, **127**, 2464 (1925); Green, *ibid.*, **129**, 500 (1926); Porter, Bardwell and Lind, *Ind. Eng. Chem.*, **18**, 1086 (1926); Funnell and Hoover, *J. Phys. Chem.*, **31**, 1099 (1927).

[14] Mohr, *Z. angew. Chem.*, **25**, 1313 (1912).

[15] Haber and Le Rossignol, *Ind. Eng. Chem.*, **5**, 328 (1913).

[16] Chaudron, *Compt. rend.*, **172**, 152 (1921).

[17] *Wied. Ann.*, **34**, 623 (1888); **36**, 346 (1889).

[18] *Ber. physik. Ges.*, **10**, 814 (1908); **11**, 237 (1909).

The methods for the analysis of gases which depend upon the change of thermal conductivity are based upon the following principle. If a wire is surrounded by a gas which is contained in a chamber whose walls are maintained at constant temperature, the temperature of the wire will, when a constant current is passed through it, rise until a point is reached at which the heat supplied by the current is balanced by the heat conducted away from the wire. This dissipation of energy takes place by radiation, by conduction through the connections at the ends of the wire, by currents of gas circulating in the space surrounding the wire, by the passage of gas if there is a flow of gas past the wire, and by conduction through the gas.

[19] *Physik. Zeit.*, **12**, 417 (1911).

[20] *Physik. Zeit.*, **12**, 1101 (1911).

[21] Moeller, *Chem. Ztg.*, **46**, 595 (1922).

[22] Shakespear and Daynes, *Proc. Roy. Soc.*, London, **97A**, 273 (1920); *Ind. Eng. Chem.*, **12**, 1027 (1920).

[23] Weaver, Palmer, Frantz, Ledig and Pickering, *Ind. Eng. Chem.*, **12**, 359 (1920); Weaver and Palmer, *ibid.*, **12**, 894 (1920); Weaver, *ibid.*, **12**, 1027 (1920); Weaver and Palmer, *Bureau of Standards, Tech. Paper* No. 249 (1924).

Only a small portion of the total dissipation of energy is due to radiation if the temperature of the wire does not exceed 400°. If the distance between the wire and the surrounding walls is not greater than 5 mm., dissipation by convection is also very small. Hence it is obvious that by proper arrangement of the conditions, all loss of heat except by conduction through the gas that surrounds the wire can be rendered negligible, and under such circumstances the temperature attained by the wire will depend mainly upon the thermal conductivity of the gas that surrounds the wire; the temperature will be lower if the gas has a high conductivity, and higher when the gas has a low conductivity. Although the thermal conductivity of gases is very much less than that of solids or liquids, it is nevertheless of appreciable magnitude, as may be seen from the values given in Table XX.

If now the wire has a high temperature coefficient of electrical resistance, this resistance will have a value corresponding to the thermal conductivity of the surrounding gas mixture and therefore to its composition.

The determination of the conductivity of a gas in absolute units is difficult. It is, however, a comparatively simple matter to make an indirect comparison between the conductivity of the gas mixture under analysis and some other gas, "reference gas." By comparison of the resistance of two wires surrounded respectively by the reference gas and a mixture of two gases of which the composition is qualitatively known, the percentages of the two gases in the mixture can rapidly and accurately be quantitatively determined after an empirical calibration has been made. The accuracy of the determination will depend on the regulation of the temperature, the rate of gas flow, the applied e. m. f., and the precision of the measuring instrument.

This comparison is most simply made by some form of Wheatstone bridge. Generally the two wires to be compared

TABLE XX[24]

THERMAL CONDUCTIVITIES OF GASES AND VAPORS

K is the heat in gram-calories flowing per second through an area of 1 sq. cm. with a temperature gradient of 1° C. per cm.

GAS OR VAPOR	0° C.		100° C.	
	$K \times 10^4$	$\frac{K\ gas}{K\ air}$	$K \times 10^4$	$\frac{K\ gas}{K\ air}$
Air	0.566	1.00	0.719	1.00
Ammonia	0.458	.81 1.15*	0.709	.98
Argon	0.388	.686 .676*	0.509	.708
Benzene		.405*		
Carbon dioxide	0.332	.585 .625*	.0496	.690 .760*
Carbon disulphide		.312*		
Carbon monoxide	0.542	.958 .936*		
Chlorine		.370*		
Chloroform		.273*		
Ethane	0.496	.876		
Ethyl alcohol		.708*		
Ethyl bromide		.607*		
Ethylene	0.395	.698	0.636	.885
Ethylene chloride		.718*		
Ethyl ether		.582*		
Helium	3.44	6.08 6.34*	3.98	5.53
Hydrogen	4.16	7.35 6.88*	4.99	6.94 6.68*
Hydrogen chloride		.635*		
Hydrogen sulphide		.648*		
Methane	0.720	1.127		
Methyl alcohol		1.314*		
Nitric oxide	0.46†	.812†		
Nitrogen	0.568	1.004	0.718	.999 .995*
Nitrous oxide	0.353	.624		
Oxygen	0.570	1.007 1.002*	0.743	1.034 1.013*
Sulphur dioxide		.415*		
Water vapor				1.05*

* These values have been computed from miscellaneous data on specific heats and viscosities and should not be regarded as more than approximations.

† These values are at 8° C.

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[24] From *Bureau of Standards, Tech. Paper* No. 249 (1924).

are connected in series in two adjacent arms of the bridge as shown in Fig. 106.

In this unbalanced arrangement of a Wheatstone bridge, the two wires of the thermal conductivity unit *A* and *B* form two arms of the bridge, and the other two arms are fixed resistances R_1 and R_2. A sensitive, low-reading voltmeter *D* may be used as an indicating instrument, and *S* is a variable resistance employed in calibrating the instrument. A potentiometer may be used in place of the voltmeter *D*. *E* is a source of e. m. f., which must be constant because the resistances of the wires *A* and *B* are affected very materially by changes in the current strength. A storage battery is very satisfactory as its use avoids the necessity of frequent adjustment. Some provision should be made for recharging it or for always keeping it fully charged. The latter arrangement is preferable if the apparatus is of the recording type and is used continuously. In this arrangement, the resistances R_1 and R_2 should be such that the bridge is balanced when the constituent to be determined in the gas that surrounds *A* is at the lowest concentration to be expected in the analysis. As the thermal conductivity of the gas changes with changes in its composition, the wires *A* and *B* will lose heat at different rates. This results in a difference of temperature and consequently in a difference of resistance which in turn causes the bridge to be unbalanced. The indicator *D* will show a deflection the extent of which will indicate directly the percentage of the variable constituent after the calibration has been made.

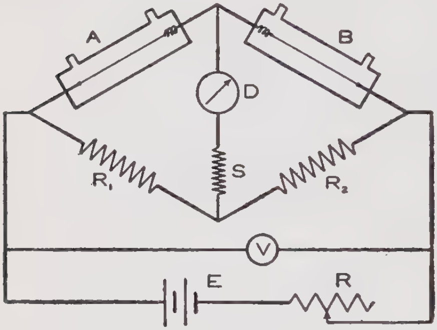

Fig. 106

Instead of the above arrangement, a calibrated slide wire together with external resistances may be used as the ratio arms of the bridge (Fig. 107).

In this case the bridge is balanced by moving the contact on the slide wire until the galvanometer *G* gives a zero reading. From the calibration, the position of the contact on the slide wire is an indication of the relative resistances of the two wires and of the amount of the constituent to be determined in the gas mixture. By substituting for *G* an alternating current galvanometer, the use of alternating current is possible.

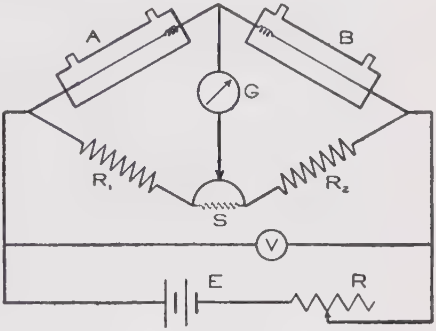

FIG. 107

Of these arrangements the first is the simplest, but the latter is more flexible; but each has its own advantages and limitations and can usually be made to give satisfactory service.

In the katharometer, Shakespear[25] used a thermal conductivity unit in which two small helices of thin platinum wire are enclosed each in one of two cells in a copper block to serve as the two arms of the Wheatstone bridge. The Bureau of Standards, as a result of their investigation to develop an easily constructed, rugged unit, has recommended the form shown in Fig. 108.

A is a platinum wire of 0.05 mm. diameter and 100 mm. long. It should be of good quality because even slight impurities may greatly reduce the temperature coefficient of resistance. To one end of the platinum wire is fused a 0.025 cm. (No. 30) copper wire *B*, 5 cm. in length and wound into a helical spring. This is fused to a 0.129 cm. (No. 16) copper wire *C*. The helical spring serves to keep the platinum wire stretched along the axis of the cell regardless of the elongation of the platinum wire when heated by the electrical current. The other end of the platinum wire is soldered with gold to a 0.064 cm. (No. 22) platinum wire, *D,* 3 cm. long. The gas chamber *E* in which the platinum wire is stretched is a cylindrical hole 10 mm. in diameter drilled lengthwise through a rolled brass or copper bar 12.5 mm. square and 125 mm. long. This chamber is provided with inlet and outlet copper tubes *F* and *G* for the circulation of the gas. These are soldered with silver to the openings provided for them. The copper terminal *C* is soldered to a bushing which closes the bottom of the cell; the platinum terminal *D* at the top is insulated from the walls of the cell by a small glass sleeve fused to it. A small platinum tube is fused over the outside of the glass sleeve and this is soldered to a bushing which closes the top of the cell. A metal cap is used to project this glass platinum seal from injury. The insulating joints devised by the Geophysical Laboratory[26] may be used. This type of insulating joint permits the insertion, as a unit, of a separately mounted platinum wire in the gas chamber used by Shakespear. The cell may also be constructed of glass for use with a highly corrosive gas such as chlorine. Two such units are necessary, and if they are carefully constructed no further compensation for changes in temperature are needed unless a high degree of accuracy is essential. Since, however, the rate at which the heat is

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[25] *Loc. cit.*

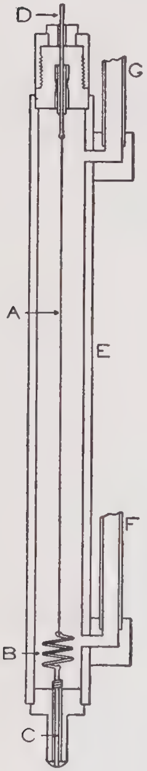

Fig. 108

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[26] Johnston and Adams, *Am. J. Sci.,* **31**, 506 (1911).

conducted through the gas in the cell depends not only on the conductivity of the gas but also upon the difference in temperature between the wires and the cell walls, it is frequently necessary to mount the units in an electrically heated oil- or air-bath thermostat.

It has been pointed out that some heat may be carried away by the flow of the gas past the wires of the thermal conductivity units. However, it has been found that this apparatus is independent of the rate of flow of gas from 0 to 20 cc. per minute, but a very rapid flow will introduce an error. To reduce the lag between a change in the composition of the gas and the corresponding indication, it is sometimes advantageous to sweep out the sampling line with a strong current of gas and to by-pass into the unit what is needed for analysis.

The thermal conductivity of a gas is independent of its pressure,[27] but the resistance of the wire may be affected by changes in the pressure of the surrounding gas. However, variations in pressure up to several centimeters of mercury do not materially affect the accuracy of the thermal conductivity method unless they are accompanied by great variations in the rate of flow of the gas past the heated wires.

Calibration.—The values represented by the readings of this device can be known only if the apparatus is empirically calibrated under conditions which duplicate those of actual service. This is usually done by preparing and carefully analyzing gas mixtures having the same constituents as those with which the apparatus is to be used. Such a gas mixture is passed through one of the units, and the reference gas is passed through the other. Air and hydrogen are generally used as reference gases, air being employed when the mixture has a low conductivity, and hydrogen when the conductivity of the mixture is high. The relation between the potential drop across the bridge and the composition of the gas is not exactly linear, although the departure from a straight line is not very great over small ranges of variation in the composition of the gas mixture. Therefore if the limit of variation of a constituent of a gas mixture is small, the indications of the apparatus are approximately linear functions of the volume percentages of the constituent, and in such cases it is only necessary to locate experimentally two points on the scale. In other cases where the displacement of the indicator is not a linear function of the composition of the gas, several gas mixtures must be used to properly calibrate the apparatus.

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[27] Gregory and Archer, *Phil. Mag.*, [7] **1**, 593 (1926).

Unbalanced Bridge.—In calibrating the unbalanced bridge arrangement shown in Fig. 106, the cell *B* is filled with the reference gas. The reference gas should be either dry or saturated with moisture, depending upon whether the mixtur to be analyzed is dry or saturated. The gas mixture under examination, from which the constituent to be determined has been completely removed, is passed through cell *A* at a rate not exceeding 20 cc. per minute. The rheostat *R* is adjusted until the voltmeter *V* indicates a drop of about 2.5 volts across the bridge. The resistance of R_2 is now varied until on closing the circuit through the detecting instrument there is no deflection of the needle. An adjustable resistance *S* is then connected in series with the indicator *D*, and some of the above gas mixture which now contains a known amount of the constituent later to be determined is passed slowly through the cell *A* until it has completely displaced the first gas mixture. The resistance of S is now adjusted until the deflection of the indicator *D* corresponds to the percentage of the constituent present in the analyzed mixture. These two points are usually sufficient, but, as has already been stated, intermediate points may be determined in the same manner if desirable.

Balanced Bridge.—The calibration of the balanced bridge, Fig. 107, consists mainly in so adjusting the extension resistances R_1 and R_2 that the instrument will directly indicate the percentage of the gas to be determined. *B* is filled with the comparison gas and the pure constituent that is later to be determined is allowed to flow through *A* at a rate of 20 cc. per minute with the contact of the slide wire set at 100. When the cell *A* has been thoroughly swept out, the rheostat *R* is varied until there is a drop of about 2.5 volts across the bridge. The resistance box R_1 is set at some definite value. and R_2, which should permit readings to at least 0.1 ohm, and preferably to 0.01 ohm, is adjusted until the galvanometer *G* gives no deflection. The resistance R_1 is increased by regular intervals, and the corresponding values of R_2 for no deflection of the galvanometer are determined. The pure gas in *A* is then completely replaced by a carefully analyzed mixture corresponding to the lower limit of the constituent, and, with the slide wire contact set at a scale division corresponding to the percentage of the constituent that is present, another series of correct end resistances is determined as above. These values are then plotted, using the resistances of one box as ordinates and of the other as abscissas, and the intersection of the two curves gives the values of R_1 and R_2 to be used for this range of variation of the constituent for the determination of which the instrument is being calibrated. The shunt *S* is used to bring the value of the end coils to the same order of magnitude as the resistance of the thermal conductivity units, for this gives higher sensitivity and uniformity of electrical characteristics.

Applications.—The thermal conductivity method for the analysis of gas mixtures is limited in its usefulness by the fact that the indications obtained can be interpreted only by means of a previous calibration under conditions closely approximating those of actual service. Therefore the method can give no information regarding the qualitative composition of an unknown mixture of gases, and it is of little or no value for the occasional examination of isolated samples of gas. Its principle use is for observing and recording changes in the composition of mixtures of which the qualitative composition and the limiting amounts of the different constituents that may be present are known.

The method possesses high sensitivity for the analysis of binary mixtures by comparison with a standard gas, when the two components differ materially in thermal conductivity. Examples of this are the determination of hydrogen in electrolytic oxygen, oxygen in electrolytic hydrogen, hydrogen in electrolytic chlorine, helium in mixtures of helium and nitrogen, and hydrogen in nitrogen. It may also be applied to the determination of the amount of a gas that is present in a mixture of gases of known composition, as, for example, for the determination of hydrogen in air. It may also be used for the determination of a single gas in a mixture when this constituent has a thermal conductivity widely different from that of the other gases present. Examples of this are the determination of hydrogen in water-gas, or in a mixture of hydrogen, nitrogen, and carbon monoxide, the determination of carbon dioxide in flue gas, the determination of sulphur dioxide in burner gases, and the determination of hydrogen or helium in gas mixtures used for filling balloons.

Another important application of this method is for the determination of a constituent in a gas mixture by the comparison of the mixture before and after the removal of the constituent by absorption in a suitable reagent, or by subjecting the mixture to some process which will cause the removal or a chemical change of the gas in question. Examples of such analyses are the determination of ammonia in mixtures of hydrogen and nitrogen, of carbon dioxide or of methane in air, and the determination of atmospheric gases in hydrogen.

The use of this method may also be extended by adding a known amount of some gas to a mixture, and then comparing, by one of the above methods, the mixture before and after the removal of the constituent that is to be determined. This method applies to the determination of oxygen in flue gas; hydrogen is added to the gas mixture and the oxygen is then determined.

Carbon monoxide may be determined in the presence of large amounts of hydrogen by first removing any oxygen that may be present, and then adding pure oxygen and burning over copper oxide in a small combustion tube. The carbon dioxide that is formed is absorbed in a solution of caustic soda. A volume of hydrogen equivalent to the oxygen added is then added and the mixture is passed through a combustion tube similar to the first one which removes the excess of oxygen. Since the combustible gases are replaced by hydrogen, a comparison of the gas mixture before and after the double burning gives the carbon monoxide present.

It is also possible to make many combinations of the above-described methods to increase the applications of the thermal conductivity method.

VAPOR PRESSURE, FRACTIONAL DISTILLATION AT LOW TEMPERATURES AND PRESSURES

The first important study of the separation of gases by fractional distillation at low temperature was that of Ramsay and Travers.[28] Their investigation, however, was confined chiefly to the rare gases of the atmosphere and to the preparation of pure gases. Yet Travers [29] does mention the separation of ethylene from carbon monoxide by this method. Dewar [30] recommended the use of this procedure in gas analysis, and later Erdmann and Stoltzenberg [31] modified the apparatus of Travers and applied the method to the separation of other mixtures. Lebeau and Damiens [32] also separated gases by this procedure and were the first to ascertain the temperatures at which pairs of the paraffin and olefine hydrocarbons could be separated. Burrell, Siebert, and Robertson [33] used a method similar to that of Ramsay to determine the constituents of natural gas and of illuminating gas, and they ascertained the vapor pressures of different gases at low temperatures. Hamburger and Filippo [34] used this method to determine the composition of mixtures of argon and nitrogen, and Wollers [35] employed it for the determination of hydrocarbons in industrial gases. Shepard and Porter [36] found that with the method and apparatus of Burrell and his co-workers, it required almost a week to secure an accurate separation of some gas mixtures, and they materially shortened the procedure. The fractional distillation of gases has been thoroughly studied by Stock,[37] who devised a special mercury valve of unique design (see p. 110) and employed the procedure in the study of the hydrides of boron and of silicon. His apparatus in modified form has been used by Dennis [38] and his co-workers in the study of the hydrides of germanium.

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[28] *Proc. Roy. Soc.*, London, **63**, 437 (1898); **64**, 183 (1898); *Phil. Trans.*, **197**, 47 (1901); Travers, *Experimental Study of Gases* (1901), p. 212.

[29] *Op. cit.*, p. 211.

[30] *Chem. News*, **80**, 187 (1899).

[31] *Ber.*, **43**, 1702, 1708 (1910).

[32] *Compt. rend.*, **156**, 144, 325, 797 (1913); *Ann. chim.*, **8**, 221 (1917); Lebeau and Marmasse, *Compt. rend.*, **180**, 1847 (1925); Czako, *J. Gasbel.*, **56**, 1172 (1913).

In the separation of gases by fractional distillation, the gas mixture must first be liquefied. The different constituents are then separated by successive distillations at temperatures at which the most volatile constituent present has an appreciable vapor pressure, and the less volatile components have negligible vapor pressures. The distillation is accomplished either by cooling the receiving bulb to a temperature at which the distillate will rapidly be liquefied or solidified, or by removing the volatilizing constituent with a pump.

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[33] *J. Am. Chem. Soc.*, **36**, 1537 (1914), **37**, 392 2188, 2482 (1915); *Ind. Eng. Chem.*, **7**, 17, 112, 209, 210, 669 (1915); *Bureau of Mines, Tech. Paper* No. 104 (1915), No. 142 (1916); Whiton, *Ind. Eng. Chem.*, **8**, 733 (1916); Anderson, *ibid.*, **9**, 142 (1917); Burrell and Jones, *ibid.*, **8**, 735 (1918).

[34] *Z. angew. Chem.*, **28**, 75 (1915).

[35] *Z. angew. Chem.*, **35**, 536 (1922).

[36] *Ind. Eng. Chem.*, **15**, 1143 (1923).

[37] *Ber.*, **49**, 111 (1916); **50**, 989 (1917); **54**, 142 (1921); *Z. Elektrochem.*, **23**, 33 (1917).

[38] Dennis, Corey and Moore, *J. Am. Chem. Soc.*, **46**, 657 (1924); Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1043 (1926).

Burrell, Siebert, and Robertson[39] have employed this method of separation in the analysis of natural gas and illuminating gas.

The boiling points of the different constituents of artificial and natural gas, and the temperatures at which they can be separated, are given in Table XXI.

TABLE XXI[40]

Gas	Boiling Point °C.
Distillate at Temperature of Liquid Air	
Carbon monoxide	—190
Hydrogen	—253
Methane	—160
Nitrogen	—195
Oxygen	—183
Distillate at —150° to —140°	
Ethylene	—103
Ethane	—93
Distillate at —135° to —120°	
Propane	—45
Propylene	—51
Distillate at — 78°	
N-Butane	1
Isobutane	—10
Isobutylene	—4
Residue at — 78°	
Benzene	80

Shepard and Porter[41] have designed an apparatus which combines in one unit the parts that are necessary for the condensation, distillation, pumping, storage, measurement of volume, and distribution of the gases. This apparatus is similar in principle to that described by Laubengayer and

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[39] *Loc. cit.*

[40] From *Bureau of Mines, Tech. Paper* No. 104 (1915).

[41] *Loc. cit.*

Corey[42] except that the latter employs the mercury float valves devised by Stock instead of stopcocks, a modification that eliminates the possibility of the gases either being adsorbed by or reacting with the lubricant on the stopcock.

DIFFUSION

Fractional diffusion has been utilized by numerous investigators[43] for the separation of the constituents of a gas mixture.

OTHER METHODS

In addition to these physical methods of analysis, there may be mentioned the interesting procedure of Thomson involving the use of positive rays,[44] and that of Geberth which is based upon variations in resonance.[45]

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[42] *Loc. cit.*

[43] Ramsay and Rayleigh, *Phil. Trans.*, **186**, 187 (1895); Ramsay and Collie, *Proc. Roy. Soc.*, **60**, 206; Ramsay and Travers, *ibid.*, **60**, 306; Travers, *Experimental Study of Gases* (1901), p. 288; Hertz, *Physik. Zeit.*, **23**, 433 (1922); Lorenz and Magnus, *Z. anorg. allgem. Chem.*, **136**, 97 (1924).

[44] J. J. Thomson, *Rays of Positive Electricity and their Application to Chemical Analysis* (1913); F. W. Aston, *Isotopes* (1922).

[45] Geberth, *Ind. Eng. Chem.*, **15**, 1277 (1923).

CHAPTER XXII

MICRO-ANALYSIS OF GASES

The accurate analysis of very small quantities of gases is impossible in the ordinary forms of gas volumetric apparatus, and this has led to the development of special devices for making such analyses. The numerous appliances may be divided into two general classes: those that depend upon the measurement of the pressures exerted by the gas mixture in a constant volume of fair magnitude, and those in which the gas volume is measured at atmospheric or constant pressure in a calibrated capillary tube.

Method of Constant Volume.—The majority of the forms of apparatus for this method are based upon the principle[1] that the relation between the vapor pressure p of a substance and the temperature T can be represented approximately by

$$\log p = A - \frac{B}{T - T_0}$$

which gives

$$\frac{ldp}{pdT} = \frac{(\log p - A)^2}{B^2}$$

Hence $\frac{ldp}{pdT}$ becomes infinite as the vapor pressure approaches zero at the temperature T_0 which is termed the condensation temperature and which is characteristic of the gas. The least change of pressure which any gauge will register is fixed by the value dp/p. Measurement of the vapor pressure thus makes it possible to determine the temperature T_0 and in this manner to identify the gas.

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[1] Campbell, *Proc. Phys. Soc.*, London, **33**, 287 (1921).

If several condensable gases but no permanent gases are present, and the temperature is increased from below T_0 for the least condensable gas, a vapor-pressure temperature curve will be obtained, as shown in Fig. 109. In such a curve, the sudden rises serve to identify the gases, and the change in the ordinates $o - p^1$, $p^1 - p^2$, etc., gives the quantity of the gases if the calibration curves are known. If any permanent gases are present, the same type of curve is obtained but it is raised above the horizontal axis by a distance corresponding to the amount of such gases present.

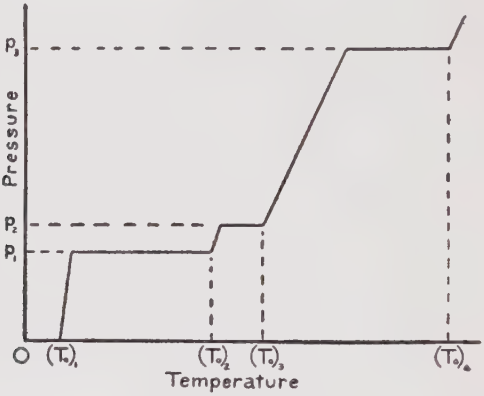

FIG. 109

Various forms of apparatus for the micro-analysis of gases by the method of constant volume have been employed by Langmuir,[2] Ryder,[3] Hamburger and Koopman,[4] and Campbell.[5] In each case the entire apparatus is exhausted and the gas sample is introduced. The condensable gases are solidified in a small bulb that is surrounded by liquid air, and the pressure of the permanent gases is determined by a suitable gauge. The McLeod gauge (see Chapter III) has been used, but Campbell recommends the Pirani gauge[6] for measurement of these low pressures. The permanent gases are then pumped off with a Töpler pump (see p. 8) and are stored[7] for further analysis after the completion of the analysis of the condensable gases. Automatic pumps of the Sprengel type have also been used, but with this type some gas may be occluded[8] by the mercury.

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[2] *J. Am. Chem. Soc.*, **34**, 1310 (1912).
[3] *Ibid.*, **40**, 1656 (1918).
[4] *Z. anal. Chem.*, **57**, 121 (1918).
[5] *Loc. cit.*

Campbell describes[9] his procedure as follows: "If a qualitative analysis of the gases is being made, the best and most convenient way to identify the vapours is not to use any thermometer of an ordinary type but to compare the T_0's of the unknown mixture with the T_0's of known vapours. A series of gauges may be made up containing between them all the vapours likely to be present; any gauge of this series may, of course, contain more than one vapour so long as no interaction between constituents can occur. The side tubes from the series of known vapours and the side tube from the gauge under analysis are then immersed in a little mercury in a small Dewar flask, and liquid air poured in until the whole is cooled to the temperature of that liquid. The conductivity of the mercury is sufficient to maintain all the side tubes at the same temperature. The mercury is then warmed by blowing air at a suitable rate on its surface, and the unknown gauge watched until a sudden change in (V^2) occurs. The air stream is then stopped temporarily and the known gauges examined to discover in which of them (V^2) has changed. If several have changed from their liquid air values the constituent in the unknown gauge is, of course, that one in these known gauges which has the highest T_0.

"This method is extraordinarily sensitive and certain. One per cent of water in CO_2 may be detected, an unfavourable case because the main constituent evaporated before the impurity; 0.0005 mm. of CO_2 may be detected in an unlimited quantity of vapours with higher T_0, or in 0.05 mm. of permanent gases. On the other hand, mercury vapour is not easy to detect. Apparently its cooling effect is very small. But it is usually known without analysis whether mercury is present, and, if so, how much.

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[6] Hale, *Trans. Am. Electrochem. Soc.*, **20**, 243 (1911).
[7] Manley, *Proc. Phys. Soc.*, London, **38**, 129 (1926).
[8] Hamburger and Koopman, *loc cit.*
[9] *Loc. cit.*

"If the constituents are known, the estimate of their amounts can be made very rapidly. A series of baths are prepared at temperatures which lie between the T_0's for the constituents; the side tube is then placed in the baths in succession, and the change in (V^2) in passing from one bath to another gives the amount of the vapour with a T_0 between the temperatures of the two baths.

"After the values of V have been measured with the side tube immersed in the various baths, the side tube is opened and sealed to a pump, and V_0 measured when the gauge is completely exhausted. If accuracy is required, V_0 must be measured while the gauge is still on the pump, for in sealing it off, a small quantity of water vapour is always liberated from the melted glass. It is desirable for accuracy that the whole process should be completed as quickly as possible, in order that the room temperature may not change. It can be completed quite easily with practice in half an hour, and with reasonable care the variations during that time are not likely to be important. The most important source of error lies in the assumption, necessary unless very elaborate calculations are to be made, that the calibration curves are all straight and that the value of (V^2) for a mixture is the sum of those for its constituents. The truth of these two assumptions is probably closely connected."

Campbell states that there is no difficulty due to the vapor pressure of one gas not rising from zero to a maximum in the interval between T_0 for that gas and T_0 for the gas of the next higher condensation temperature.

After the completion of the analysis of the condensable gases, the permanent gases may be converted by combustion into condensable gases, and these then returned to the apparatus and analyzed by the same method.

With the forms of apparatus described by Guye and Germann,[10] Chamberlin and Newitt,[11] and Prescott,[12] the constituents are absorbed by chemical reagents and the change of pressure is noted.

Method of Constant Pressure.—This method was first used by Timiriazeff[13] for the analysis of mixtures of carbon dioxide and oxygen. More recently Reeve[14] and Christiansen[15] have described forms of apparatus whereby complete analyses may be carried out by this method. The gas constituents are determined by absorption and combustion as in the ordinary methods of macro-analysis, with modifications necessary for handling very small quantities of gas.

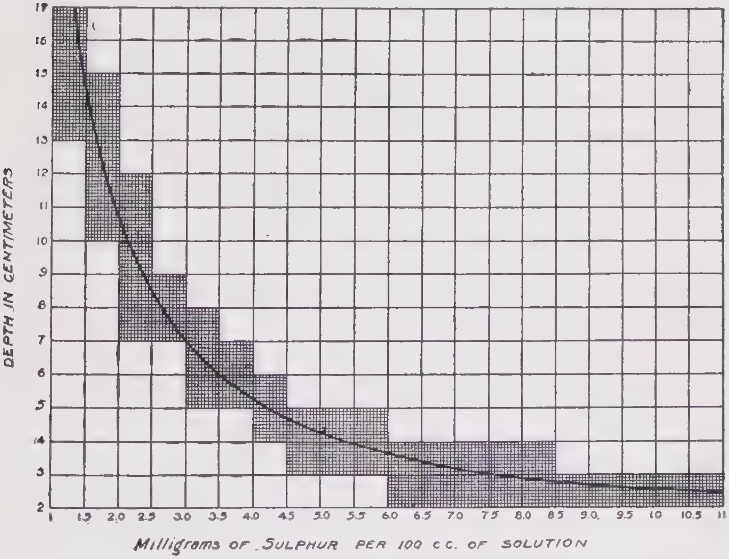

Fig. 110. (See p. 359.)

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[10] *Compt. rend.*, **159**, 154 (1914).
[11] *Ind. Eng. Chem.*, **17**, 621 (1925).
[12] *J. Am. Chem. Soc.*, **50**, 3237 (1928).
[13] *Ann. chim. phys.*, [**5**], **12**, 355 (1877).
[14] *J. Chem. Soc.*, **125**, 1946 (1924).
[15] *J. Am. Chem. Soc.*, **47**, 109 (1925).

APPENDIX

Atomic Weights, 1928

	Symbol	Atomic Weight		Symbol	Atomic Weight
Aluminum	Al	26.97	Mercury	Hg	200.61
Antimony	Sb	121.77	Molybdenum	Mo	96.0
Argon	A	39.94	Neodymium	Nd	144.27
Arsenic	As	74.96	Neon	Ne	20.183
Barium	Ba	137.37	Nickel	Ni	58.69
Beryllium	Be	9.02	Nitrogen	N	14.008
Bismuth	Bi	209.00	Osmium	Os	190.8
Boron	B	10.82	Oxygen	O	16.000
Bromine	Br	79.916	Palladium	Pd	106.7
Cadmium	Cd	112.41	Phosphorus	P	31.027
Calcium	Ca	40.07	Platinum	Pt	195.23
Carbon	C	12.000	Potassium	K	39.096
Cerium	Ce	140.25	Praseodymium	Pr	140.92
Cesium	Cs	132.81	Radium	Ra	225.95
Chlorine	Cl	35.457	Radon	Rn	222
Chromium	Cr	52.01	Rhodium	Rh	102.91
Cobalt	Co	58.94	Rubidium	Rb	85.44
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sm	150.43
Dysprosium	Dy	162.46	Scandium	Sc	45.10
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.06
Fluorine	F	19.00	Silver	Ag	107.880
Gadolinium	Gd	157.26	Sodium	Na	22.997
Gallium	Ga	69.72	Strontium	Sr	87.63
Germanium	Ge	72.60	Sulphur	S	32.064
Gold	Au	197.2	Tantalum	Ta	181.5
Hafnium	Hf	178.6	Tellurium	Te	127.5
Helium	He	4.002	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.39
Hydrogen	H	1.008	Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	169.4
Iodine	I	126.932	Tin	Sn	118.70
Iridium	Ir	193.1	Titanium	Ti	47.90
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.9	Uranium	U	238.17
Lanthanum	La	138.90	Vanadium	V	50.96
Lead	Pb	207.22	Xenon	Xe	130.2
Lithium	Li	6.940	Ytterbium	Yb	173.6
Lutecium	Lu	175.0	Yttrium	Y	88.92
Magnesium	Mg	24.32	Zinc	Zn	65.38
Manganese	Mn	54.93	Zirconium	Zr	91.22

Theoretical Densities of Gases

and Weights of One Liter of each at 0° and 760 mm. Pressure, at Sea Level and Latitude 45°

Substance	Formula	Molecular Weight	Specific Gravity Air = 1	Density
Acetylene	C_2H_2	26.016	0.8988	1.1791
Ammonia	NH_3	17.032	0.5971	0.7708
Argon	A	39.94	1.378	1.7836
Arsine	AsH_3	77.984	2.695	3.485
Bromine	Br_2	159.832	5.5249	7.1426
Butane	C_4H_{10}	58.08	2.0065	2.6726
Butylene	C_4H_8	56.064	1.9349	2.5019
Carbon dioxide	CO_2	44.00	1.5197	1.9768
Carbon monoxide	CO	28.00	0.9673	1.2504
Carbon oxysulphide	COS	60.064	2.0752	2.721
Carbonyl chloride	$COCl_2$	98.914	3.4168	4.4172
Chlorine	Cl_2	70.914	2.4494	3.214
Cyanogen	C_2N_2	52.016	1.7968	2.3229
Ethane	C_2H_6	30.048	1.0381	1.3562
Ethylene	C_2H_4	28.032	0.9684	1.2609
Fluorine	F_2	38.00	1.31	1.695
Helium	He	4.002	0.1368	0.1785
Hydrogen	H_2	2.016	0.06965	0.08987
Hydrogen bromide	HBr	80.924	2.7973	3.6441
Hydrogen chloride	HCl	36.465	1.2684	1.6392
Hydrogen cyanide	HCN	27.016	0.9359	1.2096
Hydrogen fluoride	HF	20.008	0.713	0.894
Hydrogen iodide	HI	127.94	4.376	5.7106
Hydrogen selenide	H_2Se	81.216	2.806	3.6696
Hydrogen sulphide	H_2S	34.08	1.1773	1.5392
Hydrogen telluride	H_2Te	129.516	4.49	5.789
Krypton	Kr	82.9	2.82	3.708
Methane	CH_4	16.032	0.5545	0.7168
Methyl chloride	CH_3Cl	50.481	0.9523	2.3045
Neon	Ne	20.183	0.688	0.8999
Nitric oxide	NO	30.008	1.0367	1.3402
Nitrogen	N_2	28.016	0.96737	1.2504
Nitrogen peroxide	NO_2	46.008	1.5906	2.0563
Nitrous oxide	N_2O	44.016	1.5208	1.9777
Oxygen	O_2	32.00	1.1053	1.4290
Ozone	O_3	48.00	1.624	3.0000
Phosgene	$COCl_2$	98.914		1.435
Phosphine	PH_3	34.051	1.175	1.5293
Propane	C_3H_8	44.064	1.5204	2.0200
Propylene	C_3H_6	42.048	1.4527	1.878
Silicon tetrafluoride	SiF_4	104.06	3.60	4.693
Stibine	SbH_3	124.794	4.360	5.6
Sulphur dioxide	SO_2	64.064	2.2639	2.9267
Water vapor	H_2O	18.016	0.6218	2.8040
Xenon	Xe	130.2	4.42	5.851
Atmospheric air			1.0000	1.2930

Reduction of a Gas Volume to 0° and 760 mm.

If v is the volume of a gas at t° and p mm., pressure, the volume v_0 of the gas at 0° and 760 mm. may be calculated with the aid of the formula

$$v_0 = v \frac{p}{760\,(1 + 0.00367\,t).}$$

To facilitate the reduction of gas volumes to standard conditions, the values of the expression (1 + 0.00367 t) from — 2° to + 34° are given in the following table:

t	1 + 0.00367 t	Log $\frac{1}{1+0.00367\,t}$	t	1 + 0.00367 t	Log $\frac{1}{1+0.00367\,t}$
	0,	0,		1,	9, —10
—2°.0	99266	00320	1°.1	00404	99825
—1.9	99303	00304	1.2	00440	99809
—1.8	99339	00288	1.3	00477	99793
—1.7	99376	00272	1.4	00514	99777
—1.6	99413	00256	1.5	00551	99761
—1.5	99449	00240	1.6	00587	99746
—1.4	99486	00224	1.7	00624	99730
—1.3	99523	00208	1.8	00661	99714
—1.2	99560	00192	1.9	00697	99698
—1.1	99596	00176	2.0	00734	99682
—1.0	99633	00160		1,	9, —10
	0,	0,	2.1	00771	99666
—0.9	99670	00144	2.2	00807	99651
—0.8	99706	00128	2.3	00844	99635
—0.7	99743	00112	2.4	00881	99619
—0.6	99780	00096	2.5	00918	99603
—0.5	99816	00080	2.6	00954	99588
—0.4	99853	00064	2.7	00991	99572
—0.3	99890	00048	2.8	01028	99556
—0.2	99927	00032	2.9	01064	99540
—0.1	99963	00016	3.0	01101	99524
0.0	100000	00000		1,	9, —10
	1,	9, —10	3.1	01138	99509
+0.1	00037	99984	3.2	01174	99493
0.2	00073	99968	3.3	01211	99477
0.3	00110	99952	3.4	01248	99461
0.4	00147	99936	3.5	01285	99445
0.5	00184	99920	3.6	01321	99430
0.6	00220	99905	3.7	01358	99414
0.7	00257	99889	3.8	01395	99398
0.8	00294	99873	3.9	01431	99383
0.9	00330	99857	4.0	01468	99367
1.0	00367	99841			

Reduction of a Gas Volume to 0° and 760 mm.

Value of (1 + 0.00367 t) for t = 4.1 to 14.0°

t	1 + 0.00367 t	Log $\frac{1}{1+0.00367\,t}$	t	1 + 0.00367 t	Log $\frac{1}{1+0.00367\,t}$
	1,	9, —10		1,	9, —10
4°.1	01505	99351	9°.1	03340	98573
4.2	01541	99336	9.2	03376	98558
4.3	01578	99320	9.3	03413	98542
4.4	01615	99304	9.4	03450	98527
4.5	01652	99288	9.5	03487	98511
4.6	01688	99273	9.6	03523	98496
4.7	01725	99257	9.7	03560	98481
4.8	01762	99241	9.8	03597	98465
4.9	01798	99226	9.9	03633	98450
5.0	01835	99210	10.0	03670	98435
	1,	9, —10		1,	9, —10
5.1	01872	99195	10.1	03707	98420
5.2	01908	99179	10.2	03743	98404
5.3	01945	99163	10.3	03780	98389
5.4	01982	99148	10.4	03817	98373
5.5	02019	99132	10.5	03854	98358
5.6	02055	99117	10.6	03890	98343
5.7	02092	99101	10.7	03927	98327
5.8	02129	99085	10.8	03964	98312
5.9	02165	99070	10.9	04000	98297
6.0	02202	99054	11.0	04037	98281
	1,	9, —10		1,	9, —10
6 1	02239	99038	11.1	04074	98266
6.2	02275	99023	11.2	04110	98251
6.3	02312	99007	11.3	04147	98235
6.4	02349	98992	11.4	04184	98220
6.5	02386	98976	11.5	04221	98204
6.6	02422	98961	11.6	04257	98189
6.7	02459	98945	11.7	04294	98174
6.8	02496	98929	11.8	04331	98159
6.9	02532	98914	11.9	04367	98144
7.0	02569	98899	12.0	04404	98128
	1,	9, —10		1,	9, —10
7.1	02606	98883	12.1	04441	98113
7.2	02642	98867	12.2	04477	98098
7.3	02679	98852	12.3	04514	98083
7.4	02716	98836	12.4	04551	98067
7.5	02753	98821	12.5	04588	98052
7.6	02789	98805	12.6	04624	98037
7.7	02826	98790	12.7	04661	98022
7.8	02863	98774	12.8	04698	98006
7.9	02899	98759	12.9	04734	97991
8.0	02936	98743	13.0	04771	97976
	1,	9, —10		1,	9, —10
8.1	02973	98728	13.1	04808	97961
8.2	03009	98712	13.2	04844	97945
8.3	03046	98697	13.3	04881	97930
8.4	03083	98681	13.4	04918	97915
8.5	03120	98666	13.5	04955	97900
8.6	03156	98651	13.6	04991	97885
8.7	03193	98635	13.7	05028	97869
8.8	03230	98619	13.8	05065	97854
8.9	03266	98604	13.9	05101	97839
9.0	03303	98589	14.0	05138	97824

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0.00367\ t)$ for $t = 14.1$ to $24.0°$

t	$1 + 0.00367\ t$	Log $\frac{1}{1+0.00367\ t}$	t	$1 + 0.00367\ t$	Log $\frac{1}{1+0.00367\ t}$
	1,	9, —10		1,	9, —10
14°.1	05175	97809	19°.1	07010	97058
14.2	05211	97794	19.2	07046	97043
14.3	05248	97779	19.3	07083	97028
14.4	05285	97763	19.4	07120	97013
14.5	05322	97748	19.5	07157	96998
14.6	05358	97733	19.6	07193	96983
14.7	05395	97718	19.7	07230	96968
14.8	05432	97703	19.8	07267	96954
14.9	05468	97688	19.9	07303	96939
15.0	05505	97673	20.0	07340	96924
	1,	9, —10		1,	9, —10
15.1	05542	97657	20.1	07377	96909
15.2	05578	97642	20.2	07413	96894
15.3	05615	97627	20.3	07450	96879
15.4	05652	97612	20.4	07487	96864
15.5	05689	97597	20.5	07524	96850
15.6	05725	97582	20.6	07560	96835
15.7	05762	97567	20.7	07597	96820
15.8	05799	97552	20.8	07634	96805
15.9	05835	97537	20.9	07670	96791
16.0	05872	97522	21.0	07707	96776
	1,	9, —10		1,	9, —10
16.1	05909	97507	21.1	07744	96761
16.2	05945	97492	21.2	07780	96746
16.3	05982	97477	21.3	07817	96731
16.4	06019	97462	21.4	07854	96716
16.5	06056	97447	21.5	07891	96702
16.6	06092	97432	21.6	07927	96687
16.7	06129	97417	21.7	07964	96672
16.8	06166	97402	21.8	08001	96657
16.9	06202	97387	21.9	08037	96643
17.0	06239	97372	22.0	08074	96628
	1,	9, —10		1,	9, —10
17.1	06276	97357	22.1	08111	96613
17.2	06312	97342	22.2	08147	96598
17.3	06349	97327	22.3	08184	96584
17.4	06386	97312	22.4	08221	96569
17.5	06423	97297	22.5	08258	96554
17.6	06459	97282	22.6	08294	96539
17.7	06496	97267	22.7	08331	96525
17.8	06533	97252	22.8	08368	96510
17.9	06569	97237	22.9	08404	96495
18.0	06606	97222	23.0	08441	96481
	1,	9, —10		1,	9, —10
18.1	06643	97207	23.1	08478	96466
18.2	06679	97192	23.2	08514	96451
18.3	06716	97177	23.3	08551	96437
18.4	06753	97162	23.4	08588	96422
18.5	06790	97147	23.5	08625	96407
18.6	06826	97132	23.6	08661	96393
18.7	06863	97117	23.7	08698	96378
18.8	06900	97102	23.8	08735	96363
18.9	06936	97088	23.9	08771	96349
19.0	06973	97073	24.0	08808	96334

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0.00367\,t)$ for $t = 24.1$ to $34.0°$

t	$1+0.00367\,t$	$\text{Log}\,\frac{1}{1+0.00367\,t}$	t	$1+0.00367\,t$	$\text{Log}\,\frac{1}{1+0.00367\,t}$
	1,	9, —10		1,	9, —10
24°.1	08845	96319	29°.1	10680	95593
24.2	08881	96305	29.2	10716	95579
24.3	08918	96290	29.3	10753	95565
24.4	08955	96275	29.4	10790	95550
24.5	08992	96261	29.5	10827	95535
24.6	09028	96246	29.6	10863	95521
24.7	09065	96231	29.7	10900	95507
24.8	09102	96217	29.8	10937	95492
24.9	09138	96202	29.9	10973	95478
25.0	09175	96188	30.0	11010	95464
	1,	9, —10		1,	9, —10
25.1	09212	96173	30.1	11047	95449
25.2	09248	96159	30.2	11083	95435
25.3	09285	96144	30.3	11120	95421
25.4	09322	96129	30.4	11157	95406
25.5	09359	96115	30.5	11194	95392
25.6	09395	96100	30.6	11230	95378
25.7	09432	96086	30.7	11267	95363
25.8	09469	96071	30.8	11304	95349
25.9	09505	96057	30.9	11340	95335
26.0	09542	96042	31.0	11377	95320
	1,	9, —10		1,	9, —10
26.1	09579	96027	31.1	11414	95306
26.2	09615	96013	31.2	11450	95292
26.3	09652	95998	31.3	11487	95278
26.4	09689	95984	31.4	11524	95263
26.5	09726	95969	31.5	11561	95249
26.6	09762	95955	31.6	11597	95235
26.7	09799	95940	31.7	11634	95220
26.8	09836	95925	31.8	11671	95206
26.9	09872	95901	31.9	11707	95192
27.0	09909	95897	32.0	11744	95178
	1,	9, —10		1,	9, —10
27.1	09946	95882	32.1	11781	95163
27.2	09982	95868	32.2	11817	95149
27.3	10019	95853	32.3	11854	95135
27.4	10056	95839	32.4	11891	95120
27.5	10093	95824	32.5	11928	95106
27.6	10129	95810	32.6	11964	95092
27.7	10166	95795	32.7	12001	95078
27.8	10203	95781	32.8	12038	95064
27.9	10239	95767	32.9	12074	95049
28.0	10276	95752	33.0	12111	95035
	1,	9, —10		1,	9, —10
28.1	10313	95737	33.1	12148	95021
28.2	10349	95723	33.2	12184	95007
28.3	10386	95709	33.3	12221	94993
28.4	10423	95694	33.4	12258	94978
28.5	10460	95679	33.5	12295	94964
28.6	10496	95665	33.6	12331	94950
28.7	10533	95651	33.7	12368	94936
28.8	10570	95636	33.8	12405	94922
28.9	10606	95622	33.9	12441	94907
29.0	10643	95608	34.0	12478	94893

Tension of Aqueous Vapor[1]

Expressed in millimeters of mercury at 0°

t	Tension	t	Tension	t	Tension	t	Tension	t	Tension
° C.	mm.	° C.	mm.	° C.	mm.	° C.	mm.	° C.	mm.
−2.0	3.952	1.6	5.144	5.1	6.589	8.7	8.437	12.2	10.658
−1.9	3.981	1.7	5.181	5.2	6.635	8.8	8.494	12.3	10.728
−1.8	4.011	1.8	5.219	5.3	6.681	8.9	8.551	12.4	10.799
−1.7	4.041	1.9	5.256	5.4	6.728	9.0	8.609	12.5	10.870
−1.6	4.071	2.0	5.294	5.5	6.775			12.6	10.941
−1.5	4.101			5.6	6.822	9.1	8.668	12.7	11.013
−1.4	4.131	2.1	5.332	5.7	6.869	9.2	8.727	12.8	11.085
−1.3	4.162	2.2	5.370	5.8	6.917	9.3	8.786	12.9	11.158
−1.2	4.193	2.3	5.408	5.9	6.965	9.4	8.845	13.0	11.231
−1.1	4.224	2.4	5.447	6.0	7.013	9.5	8.905		
		2.5	5.486			9.6	8.965	13.1	11.305
−1.0	4.256	2.6	5.525	6.1	7.062	9.7	9.025	13.2	11.379
−0.9	4.287	2.7	5.565	6.2	7.111	9.8	9.086	13.3	11.453
−0.8	4.318	2.8	5.605	6.3	7.160	9.9	9.147	13.4	11.528
−0.7	4.350	2.9	5.645	6.4	7.209	10.0	9.209	13.5	11.604
−0.6	4.382	3.0	5.685	6.5	7.259			13.6	11.680
−0.5	4.414			6.6	7.309	10.1	9.271	13.7	11.756
−0.4	4.447			6.7	7.360	10.2	9.333	13.8	11.833
−0.3	4.480	3.1	5.725	6.8	7.411	10.3	9.395	13.9	11.910
−0.2	4.513	3.2	5.766	6.9	7.462	10.4	9.458	14.0	11.987
−0.1	4.546	3.3	5.807	7.0	7.513	10.5	9.521		
		3.4	5.848			10.6	9.585	14.1	12.065
0.0	4.579	3.5	5.889	7.1	7.565	10.7	9.649	14.2	12.144
+0.1	4.613	3.6	5.931	7.2	7.617	10.8	9.714	14.3	12.223
0.2	4.647	3.7	5.973	7.3	7.669	10.9	9.779	14.4	12.302
0.3	4.681	3.8	6.015	7.4	7.722	11.0	9.844	14.5	12.382
0.4	4.715	3.9	6.058	7.5	7.775			14.6	12.462
0.5	4.750	4.0	6.101	7.6	7.828	11.1	9.910	14.7	12.543
0.6	4.785			7.7	7.882	11.2	9.976	14.8	12.624
0.7	4.820	4.1	6.144	7.8	7.936	11.3	10.042	14.9	12.706
0.8	4.855	4.2	6.187	7.9	7.990	11.4	10.109	15.0	12.788
0.9	4.890	4.3	6.230	8.0	8.045	11.5	10.176		
1.0	4.926	4.4	6.274			11.6	10.244	15.1	12.870
		4.5	6.318	8.1	8.100	11.7	10.312	15.2	12.953
1.1	4.962	4.6	6.363	8.2	8.155	11.8	10.380	15.3	13.037
1.2	4.998	4.7	6.408	8.3	8.211	11.9	10.449	15.4	13.121
1.3	5.034	4.8	6.453	8.4	8.267	12.0	10.518	15.5	13.205
1.4	5.070	4.9	6.498	8.5	8.323			15.6	13.290
1.5	5.107	5.0	6.543	8.6	8.380	12.1	10.588	15.7	13.375

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[1] Landolt-Börnstein, *Physikalisch-Chemische Tabellen* (1923), p. 1316. From measurements by Scheel and Heuse, *Ann. d. Phys.*, [4] 31, 715 (1910).

Tension of Aqueous Vapor.—*Continued*

t	Tension	t	Tension	t	Tension	t	Tension	t	Tension
° C.	mm.	° C.	mm.	° C.	mm.	° C.	mm.	° C.	mm.
15.8	13.461	**19.4**	16.894	**23.1**	21.196	**26.8**	26.426	**30.4**	32.561
15.9	13.547	**19.5**	16.999	**23.2**	21.324	**26.9**	26.582	**30.5**	32.747
16.0	13.634	**19.6**	17.105	**23.3**	21.453	**27.0**	26.739	**30.6**	32.934
		19.7	17.212	**23.4**	21.583			**30.7**	33.122
16.1	13.721	**19.8**	17.319	**23.5**	21.714	**27.1**	26.897	**30.8**	33.312
16.2	13.809	**19.9**	17.427	**23.6**	21.845	**27.2**	27.055	**30.9**	33.503
16.3	13.898	**20.0**	17.535	**23.7**	21.977	**27.3**	27.214	**31.0**	33.695
16.4	13.987			**23.8**	22.110	**27.4**	27.374		
16.5	14.076	**20.1**	17.644	**23.9**	22.243	**27.5**	27.535	**31.1**	33.888
16.6	14.166	**20.2**	17.753	**24.0**	22.377	**27.6**	27.696	**31.2**	34.082
16.7	14.256	**20.3**	17.863			**27.7**	27.858	**31.3**	34.276
16.8	14.347	**20.4**	17.974	**24.1**	22.512	**27.8**	28.021	**31.4**	34.471
16.9	14.438	**20.5**	18.085	**24.2**	22.648	**27.9**	28.185	**31.5**	34.667
17.0	14.530	**20.6**	18.197	**24.3**	22.785	**28.0**	28.349	**31.6**	34.864
		20.7	18.309	**24.4**	22.922			**31.7**	35.062
17.1	14.622	**20.8**	18.422	**24.5**	23.060	**28.1**	28.514	**31.8**	35.261
17.2	14.715	**20.9**	18.536	**24.6**	23.198	**28.2**	28.680	**31.9**	35.462
17.3	14.809	**21.0**	18.650	**24.7**	23.337	**28.3**	28.847	**32.0**	35.663
17.4	14.903			**24.8**	23.476	**28.4**	29.015		
17.5	14.997	**21.1**	18.765	**24.9**	23.616	**28.5**	29.184	**32.1**	35.865
17.6	15.092	**21.2**	18.880	**25.0**	23.756	**28.6**	29.354	**32.2**	36.068
17.7	15.188	**21.3**	18.996			**28.7**	29.525	**32.3**	36.272
17.8	15.284	**21.4**	19.113	**25.1**	23.897	**28.8**	29.697	**32.4**	36.477
17.9	15.380	**21.5**	19.231	**25.2**	24.039	**28.9**	29.870	**32.5**	36.683
18.0	15.477	**21.6**	19.349	**25.3**	24.182	**29.0**	30.043	**32.6**	36.891
		21.7	19.468	**25.4**	24.326			**32.7**	37.099
18.1	15.575	**21.8**	19.587	**25.5**	24.471	**29.1**	30.217	**32.8**	37.308
18.2	15.673	**21.9**	19.707	**25.6**	24.617	**29.2**	30.392	**32.9**	37.518
18.3	15.772	**22.0**	19.827	**25.7**	24.764	**29.3**	30.568	**33.0**	37.729
18.4	15.871			**25.8**	24.912	**29.4**	30.745		
18.5	15.971	**22.1**	19.948	**25.9**	25.060	**29.5**	30.923	**33.1**	37.942
18.6	16.071	**22.2**	20.070	**26.0**	25.209	**29.6**	31.102	**33.2**	38.155
18.7	16.171	**22.3**	20.193			**29.7**	31.281	**33.3**	38.369
18.8	16.272	**22.4**	20.316	**26.1**	25.359	**29.8**	31.461	**33.4**	38.584
18.9	16.374	**22.5**	20.440	**26.2**	25.509	**29.9**	31.642	**33.5**	38.801
19.0	16.477	**22.6**	20.565	**26.3**	25.660	**30.0**	31.824	**33.6**	39.018
		22.7	20.690	**26.4**	25.812			**33.7**	39.237
19.1	16.581	**22.8**	20.815	**26.5**	25.964	**30.1**	32.007	**33.8**	39.457
19.2	16.685	**22.9**	20.941	**26.6**	26.117	**30.2**	32.191	**33.9**	39.677
19.3	16.789	**23.0**	21.068	**26.7**	26.271	**30.3**	32.376	**34.0**	39.898

Tension of Aqueous Vapor [1]

Expressed in inches of mercury at 32° F.

t	Tension	t	Tension	t	Tension	t	Tension
° F.	in.	° F.	in.	° F.	in.	° F.	in.
32.0	0.180	39.4	0.242	46.6	0.319	54.0	0.420
32.2	0.182	39.6	0.244	46.8	0.321	54.2	0.423
32.4	0.183	39.8	0.246	47.0	0.324	54.4	0.426
32.6	0.185			47.2	0.326	54.6	0.429
32.8	0.186	40.0	0.248	47.4	0.329	54.8	0.433
33.0	0.188	40.2	0.250	47.6	0.331	55.0	0.436
33.2	0.189	40.4	0.252	47.8	0.334	55.2	0.439
33.4	0.191	40.6	0.254			55.4	0.442
33.6	0.192	40.8	0.256	48.0	0.336	55.6	0.445
33.8	0.194	41.0	0.258	48.2	0.339	55.8	0.449
		41.2	0.260	48.4	0.341		
34.0	0.196	41.4	0.262	48.6	0.344	56.0	0.452
34.2	0.197	41.6	0.264	48.8	0.347	56.2	0.455
34.4	0.199	41.8	0.266	49.0	0.349	56.4	0.458
34.6	0.200			49.2	0.352	56.6	0.462
34.8	0.202	42.0	0.268	49.4	0.355	56.8	0.465
35.0	0.203	42.2	0.270	49.6	0.357	57.0	0.469
35.2	0.205	42.4	0.272	49.8	0.360	57.2	0.472
35.4	0.206	42.6	0.274			57.4	0.475
35.6	0.208	42.8	0.276	50.0	0.363	57.6	0.479
35.8	0.210	43.0	0.278	50.2	0.365	57.8	0.482
		43.2	0.280	50.4	0.368		
36.0	0.212	43.4	0.282	50.6	0.371	58.0	0.486
36.2	0.213	43.6	0.285	50.8	0.373	58.2	0.489
36.4	0.215	43.8	0.287	51.0	0.376	58.4	0.493
36.6	0.217			51.2	0.379	58.6	0.496
36.8	0.219	44.0	0.289	51.4	0.382	58.8	0.500
37.0	0.220	44.2	0.291	51.6	0.385	59.0	0.503
37.2	0.222	44.4	0.294	51.8	0.388	59.2	0.507
37.4	0.224	44.6	0.296			59.4	0.510
37.6	0.225	44.8	0.298	52.0	0.390	59.6	0.513
37.8	0.227	45.0	0.300	52.2	0.393	59.8	0.517
		45.2	0.302	52.4	0.396		
38.0	0.229	45.4	0.305	52.6	0.399	60.0	0.521
38.2	0.231	45.6	0.307	52.8	0.402	60.2	0.525
38.4	0.233	45.8	0.310	53.0	0.405	60.4	0.529
38.6	0.235			53.2	0.408	60.6	0.533
38.8	0.236	46.0	0.312	53.4	0.411	60.8	0.537
39.0	0.238	46.2	0.314	53.6	0.414	61.0	0.541
39.2	0.240	46.4	0.317	53.8	0.417	61.2	0.544

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[1] These values are calculated from those given in the preceding table.

Tension of Aqueous Vapor.—*Continued*

t	Tension	t	Tension	t	Tension	t	Tension
° F.	in.	° F.	in.	° F.	in.	° F.	in.
61.4	0.548	69.6	0.729	77.8	0.960	85.6	1.237
61.6	0.552	69.8	0.734			86.0	1.253
61.8	0.556			78.0	0.966	86.2	1.261
		70.0	0.739	78.2	0.973	86.4	1.269
62.0	0.560	70.2	0.744	78.4	0.980	86.6	1.277
62.2	0.564	70.4	0.749	78.6	0.986	86.8	1.285
62.4	0.568	70.6	0.754	78.8	0.992	87.0	1.293
62.6	0.572	70.8	0.759	79.0	0.999	87.2	1.302
62.8	0.576	71.0	0.765	79.2	1.005	87.4	1.310
63.0	0.580	71.2	0.770	79.4	1.012	87.6	1.318
63.2	0.584	71.4	0.775	79.6	1.019	87.8	1.327
63.4	0.588	71.6	0.781	79.8	1.025		
63.6	0.592	71.8	0.786			88.0	1.335
63.8	0.597			80.0	1.032	88.2	1.343
		72.0	0.791	80.2	1.039	88.4	1.352
64.0	0.601	72.2	0.796	80.4	1.046	88.6	1.360
64.2	0.605	72.4	0.802	80.6	1.053	88.8	1.369
64.4	0.609	72.6	0.807	80.8	1.060	89.0	1.378
64.6	0.614	72.8	0.813	81.0	1.066	89.2	1.386
64.8	0.618	73.0	0.818	81.2	1.073	89.4	1.395
65.0	0.622	73.2	0.824	81.4	1.080	89.6	1.404
65.2	0.626	73.4	0.829	81.6	1.087	89.8	1.413
65.4	0.631	73.6	0.835	81.8	1.095		
65.6	0.635	73.8	0.841			90.0	1.422
65.8	0.640			82.0	1.102	90.2	1.430
		74.0	0.846	82.2	1.109	90.4	1.439
66.0	0.644	74.2	0.852	82.4	1.116	90.6	1.448
66.2	0.649	74.4	0.858	82.6	1.123	90.8	1.457
66.4	0.653	74.6	0.864	82.8	1.130	91.0	1.466
66.6	0.658	74.8	0.869	83.0	1.138	91.2	1.476
66.8	0.662	75.0	0.875	83.2	1.145	91.4	1.485
67.0	0.667	75.2	0.881	83.4	1.152	91.6	1.495
67.2	0.671	75.4	0.887	83.6	1.160	91.8	1.504
67.4	0.676	75.6	0.893	83.8	1.168		
67.6	0.681	75.8	0.899			92.0	1.513
67.8	0.686					92.2	1.522
		76.0	0.905	84.0	1.175	92.4	1.532
68.0	0.690	76.2	0.911	84.2	1.183	92.6	1.541
68.2	0.695	76.4	0.917	84.4	1.190	92.8	1.551
68.4	0.700	76.6	0.923	84.6	1.198	93.0	1.561
68.6	0.705	76.8	0.929	84.8	1.206	93.2	1.571
68.8	0.709	77.0	0.935	85.0	1.213	93.4	1.580
69.0	0.714	77.2	0.941	85.2	1.221	93.6	1.590
69.2	0.719	77.4	0.948	85.4	1.229	93.8	1.600
69.4	0.724	77.6	0.954	85.8	1.245	94.0	1.610

INDEX

INDEX OF AUTHORS' NAMES

A

Acree, 114
Adams, 450
Addicks, 364
Albrecht, 349
Allen, 422
Allison, 226, 304, 305
Allner, 372
Almquist, 163
Anderson, 55, 60, 66, 74, 76, 77, 85, 86, 123, 177, 178, 179, 180, 181, 185, 188, 204, 261, 363, 412, 456
Andress, 341, 342, 344
Andrews, 277
Anneler, 191, 193
Appleyard, 403
Archer, 451
Arndt, 217, 222, 386
Arnold, 190, 266
Aschof, 74
Aston, 53, 184, 458
Atkinson, 302
Aufsatz, 311
Avogadro, 134

B

Badger, 185, 186
Bähr, 344
Bailey, 46
Bain, 381
Balcon, 104
Balthaser, 315
Baly, 45
Bamberger, 193, 194, 392
Bancroft, 163
Bardwell, 444
Barkley, 315, 319, 323
Bartlett, 249
Barus, 55
Baskerville, 194, 218, 219
Baten, 381
Baudisch, 226
Baxter, 53, 55
Bayerle, 142
Beau, 280
Beckett, 27
Beckmann, 149
Bedel, 244
Behr, 400
Behrend, 280
Bell, 41
Bendemann, 74, 75
Benedict, 176, 177, 396, 403
Benton, 26
Benzant, 7
Berl, 228, 289, 290, 341, 342, 344
Bernburg, 271
Berthelot, 176
Biedermann, 184
Bieler, 403
Binder, 317, 319
Blair, 104
Bleier, 412
Bloomfield, 239, 240
Blume, 364
Bodenstein, 20
Bödlander, 428
Bolton, 113
Bone, 103
Booth, 113, 117
Boothby, 396
Bossard, 204, 362
Böttcher, 306

Boussingault, 174
Boyle, 29
Boys, 379, 381
Bradley, 110
Braun, 315, 316, 317, 319, 325
Bray, 163, 246
Bregmann, 290
Bride, 358
Brown, 363
Brügelmann, 351
Brühl, 113
Brunck, 153, 154, 202, 203, 204 240
Brunner, 181
Brünnich, 269
Buckingham, 51
Bueb, 366
Bunsen, 11, 15, 50, 91, 94, 140, 141, 173, 205
Bunte, 152, 162, 280, 372
Burdick, 224
Bürger, 344
Burgess, 88, 134
Burgstaller, 194
Burk, 48
Burke, 27, 304, 305
Burkl, 306
Burrell, 4, 74, 82, 136, 137, 141, 149, 161, 204, 219, 255, 313, 342, 362, 363, 437, 456, 457

C

Calvert, 174
Camp, 3
Campbell, 58, 60, 140, 155, 157, 201, 459, 461, 462
Carleton, 297, 301
Caro, 394
Carter, 208
Cedercreuz, 306, 388, 389
Centnerszwer, 184
Chamberlin, 463
Chapin, 425
Charles, 29
Chatterji, 444
Chaudron, 444
Christiansen, 40, 463
Christie, 298, 299, 300
Clark, 281, 290
Clausmann, 74, 245
Cloëz, 174
Clowes, 176
Cohen, 395, 403
Collie, 211, 212, 214, 458
Collins, 444
Colman, 348, 349
Colmann, 271
Cope, 432
Copp, 342
Coquillion, 143, 151
Corey, 110, 456, 458
Cramer, 248
Crittenden, 336
Crockatt, 401
Cross, 381
Crozier, 194
Crum, 422, 428
Cumming, 65
Czako, 193, 242, 280, 372, 455

D

Damiens, 243, 244, 267, 455
Daniels, 44
Davies, 246, 249, 341
Davis, 224, 344
Daynes, 445
de Castro, 159, 164
Deckert, 232
Dede, 292
de Koninck, 186
De la Condamine, 244
De la Harpe, 238
Deming, 428
Denham, 153
Dennis, 13, 56, 71, 72, 74, 76, 77, 84, 94, 110, 119, 121, 142, 143,

148, 175, 206, 319, 338, 339, 341, 346, 390, 428, 456
Desha, 114
de Smet, 123
de Voldere, 123
Dewar, 455
Dickert, 362
Dieckmann, 289
Ditte, 246
Dittmar, 301
Divers, 223
Dixon, 113
Döbereiner, 174
Dobson, 7
Dodge, 162
Doepner, 237
Doherty, 403
Dommer, 316
Donaldson, 27
Doran, 282
Doyère, 60, 94, 95, 184
Drakeley, 180
Drehschmidt, 149, 244, 245, 272, 351
Dronane, 239
Duffendack, 46
Dulong, 437
Dundon, 108
Dunglinson, 27
Dunn, 364
Dunnicliffe, 113
Dunstan, 113
Dupasquier, 279
Dürr, 316
Duschak, 117
Dykema, 363
Dyson, 303

E

Eckardt, 221, 308
Eckman, 214
Edgar, 74, 163
Edwards, 1, 51, 52, 53, 55, 142, 230, 278, 351, 438, 442, 443
Eichhorn, 215
Eisenhart, 41
Eitner, 388, 389
Elliott, 73, 245, 362
Engelder, 261, 363
Engler, 190
Erdmann, 455
Erlich, 26
Erlwein, 190
Eschmann, 214
Eucken, 445
Evans, 348

F

Fairley, 351
Fay, 55
Feder, 351, 359
Feld, 271
Ferguson, 288, 401
Fieldner, 74
Fieser, 188
Filippo, 456
Finch, 444
Fischeli, 204
Fischer, 1, 74, 190, 210, 214, 344
Flagg, 315, 319, 323
Fleissner, 65
Florentin, 237, 430
Foerster, 381
Forbes, 113
Forster, 401
Foster, 278
Fox, 209
Fraenkel, 387, 388, 393
Francis, 226
Frantz, 445
Franzen, 187
Frary, 105
Frazer, 2, 6,
Frederick, 417, 418, 419
Fresenius, 13, 157, 280, 301, 305
Frevert, 240
Friedrichs, 62, 63, 119
Friend, 215

Frischer, 242
Fritzsche, 264, 349
Froboese, 248
Fulweiler, 280
Furman, 310
Fuwa, 27

G

Gair, 349
Gale, 437
Gall, 245
Ganassini, 279
Gastaldi, 276
Gautier, 74, 245, 246
Gay, 7
Geake, 224
Geberth, 458
Geissler, 172
Geldard, 246
Germann, 44, 444, 463
Gilbert, 147, 174
Gill, 140, 249
Gille, 290
Glaser, 366
Glinzer, 379
Gmelin, 215
Göckel, 65, 91, 338
Goldschmidt, 445
Goldsmith, 7
Gollmer, 344
Gontal, 246
Goth, 174
Graham, 50, 248
Gray, 7, 20, 40, 41, 53
Grebel, 311
Green, 444
Greenwood, 172
Gregg, 100
Gregory, 451
Griggs, 27
Grob, 290
Grozea, 405
Grubbs, 276
Gruenhut, 13
Guye, 463

H

Haber, 73, 74, 135, 262, 324, 341, 343, 437, 444
Hackl, 12
Hagen, 432
Hahn, 77
Hainsworth, 243
Haldane, 177, 278, 417
Hale, 12, 461
Hall, 192, 215, 218, 222, 223, 224
Haller, 289, 290
Hamburger, 456, 460, 461
Hand, 172
Hanika, 241, 242
Hankus, 74
Hannah, 401
Harbeck, 343
Harcourt, 281, 283
Hardebeck, 26
Harding, 280, 282, 341, 351
Harger, 319
Harpster, 437, 442
Harrington, 47
Hart, 155, 201
Hartley, 246, 249, 365
Hartmann, 201, 202, 204
Hauser, 255
Hayhurst, 190, 193, 194
Hayward, 27
Hefter, 65
Hegel, 280, 282
Heinz, 74
Hempel, 4, 63, 74, 85, 94, 95, 141, 142, 149, 150, 152, 154, 155, 175, 176, 185, 199, 204, 210, 212, 216, 217, 259, 292, 294, 307, 313, 337, 338, 351, 381, 428
Henrich, 178, 187, 215
Henry, 151
Henwood, 183

Hermsdorf, 276
Herzfeld, 255
Hesse, 403
Heycock, 302
Higgins, 403
Higgs, 381
Hildebrand, 113, 114
Hinman, 362, 366
Hirsch, 351
Hofer, 172
Hoffman, 2, 6, 87, 88, 345
Hofmann, 163, 205, 240, 255, 282, 339
Hofsäss, 26, 52
Högland, 187
Holbrook, 74
Hollinger, 356
Holmes, 183
Hoover, 238
Hopkins, 143, 148, 206, 346
Hoppe-Seyler, 13
Horst, 362
Houzeau, 189
Huff, 282
Hughes, 297
Hulett, 13, 15, 112, 113, 117
Huntly 6, 313
Hurwitz, 209
Hüttner, 362
Hyde, 436

I

Ilosvay, 221, 225, 265

J

Jaeger, 73
Jäger, 157, 158, 159, 163
Japp, 427
Jefferson, 27
Jenkins, 362
Joannis, 163
Johnson, 280
Johnston, 395, 406, 408, 450
Jolly, 173
Jones, 4, 27, 73, 74, 113, 117, 141, 149, 179, 219, 226, 336, 431, 443, 456
Jordan, 214, 280
Jorissen, 349
Joseph, 27
Joyce, 431
Junkers, 366, 379, 381

K

Kaesbohrer, 422
Kaleta, 147
Kampschulte, 190
Karlsruhe, 271
Karsten, 113
Kast, 280
Katz, 205, 239, 240, 276
Kaye, 10
Keane, 58. 232. 320
Keiser, 190, 194
Kellner, 379
Keppeler, 385, 388, 389, 394
Kershaw, 7
Keyes, 8, 110
Kimball, 38
King, 72
Kinnicut, 246, 247
Klason, 291
Klemenc, 44
Klemmer, 362
Kling, 303
Klinger, 226, 227
Knop, 436
Knorre, 222
Knowland, 27
Knublauch, 349, 351
Koehler, 227
Koepsel, 444
Kohn-Abrest, 237
König, 245
Koopman, 460, 461

Kopfer, 152
Kostin, 186, 236, 237
Kowalke, 382
Krauskopf, 241
Kreidl, 286
Kreisinger, 2, 3, 7
Kreusler, 173, 174
Krieger, 342, 344
Krogh, 25
Krone, 68
Kropf, 241, 345
Krueger, 197
Kruse, 188
Kunkel, 237
Kunz-Krause, 268, 269, 276
Küspert, 339

L

Lamb, 163, 246, 297, 301
Lange, 232
Langmuir, 460
Laplace, 43
Larsen, 243
Larson, 173
Lassaigne, 308
La Tourette, 431
Laubengayer, 8, 456, 457
Lavoisier, 181
Lebeau, 244, 455
LeBlanc, 214, 221
LeChatelier, 331
Lechner, 193
Ledig, 100, 147, 150, 445
Leduc, 396
Lee, 150
Lemoult, 306
Lenger, 306
Le Rossignol, 444
Levy, 150, 238, 246
Lewes, 176, 387
Liebenthal, 336
Liebig, 174
Limpricht, 343
Lind, 444
Lindemann, 181
Lockemann, 221, 308, 309
Lomschakov, 74
Longfellow, 276
Loomis, 114
Lorah, 13
Lorenz, 458
Lowe, 73, 288
Löwe, 437
Lubberger, 171
Lundegardli, 407
Lundström, 394
Lunge, 74, 216, 221, 223, 224, 225, 228, 286, 288, 290, 306, 338, 343, 388, 389, 422, 425, 432, 436
Lux, 316

M

MacMullin, 320
McBride, 278, 335, 364
McCarthy, 339, 341
McCollister, 84
McCollum, 27
McCoy, 419
McDonnell, 194
McKee, 113, 304, 305
McKelvy, 108
McLeod, 45
McMaster, 190, 194
McWhorter, 246, 247
Macagno, 282
Magnus, 458
Mains, 114
Mallard, 331
Mams, 113
Manchot, 88, 190, 245
Manguin, 160
Manley, 461
Marchmann, 267
Marmasse, 455
Marqueyrol, 227, 430
Marriott, 403
Marsh, 24
Marx, 190

Maschmann, 266
Mase, 27
Mathers, 150
Matthews, 437
Maze, 351
Meighan, 179, 304, 305
Meldrum, 301
Melia, 12
Mendeléeff, 124
Menserve, 287
Mentzel, 190
Menzies, 444
Meyer, 74, 113, 215
Mezger, 74
Milbauer, 20
Milligan, 121, 149, 219, 224, 227, 228, 255
Minchin, 117
Misteli, 141, 205
Moeller, 197, 319, 323, 445
Mohr, 444
Moir, 276, 404
Moldenhauer, 58
Möllney, 266
Moore, 110, 113, 456
Morgan, 246, 247
Morpurgo, 379
Moser, 222, 223, 224, 225, 241, 242, 254, 306, 309
Moss, 379
Mouren, 362
Mueller, 24, 271, 366
Muenzer, 319
Müller, 74, 266, 341, 342, 344, 349
Murmann, 19, 259
Murray, 73
Myers, 108
Myhill, 52
Mylius, 362

N

Natus, 210, 214
Nauss, 270, 271
Neal, 363
Nemsjelow, 154, 159, 253
Neubeck, 341, 342
Neumann, 180
Neumeister, 74
Newcomer, 24, 25, 419
Newitt, 463
Nichols, 297
Nicloux, 237, 238, 246
Nicol, 180
Nördlander, 325
Nowicki, 74, 240, 247
Noyes, 109, 258

O

Oberfell, 74, 82, 161, 204, 362
Obermiller, 27
O'Brien, 119, 390
Odernheimer, 386
Oechelhäuser, 262, 343
Oettel, 294
Offerhaus, 298
Ogier, 237
O'Neill, 338, 339
Orsat, 73, 92
Osgood, 41
Ott, 100, 149, 161, 162, 261
Outcault, 288
Ovitz, 2, 3, 7, 145

P

Paal, 201, 202, 204, 267
Packard, 382
Palmer, 163, 445
Palmqvist, 408, 409
Paneth, 16, 215
Pannertz, 51
Parker, 141, 149, 226
Parsons, 226
Partington, 443
Patchin, 58
Patten, 113, 114
Paul, 402
Pearson, 444

Pecoul, 238
Pereira, 199
Perks, 388
Perrott, 310
Peters, 215
Peterson, 27
Petschek, 204
Pettenkofer, 403
Pettersson, 95, 100, 187, 408, 409
Petusi, 276
Pfeiffer, 72, 77, 140, 171, 339, 343
Pfund, 46
Phillips, 152, 364
Pichard, 422
Pickering, 366, 445
Piechota, 261
Pierce, 27, 336
Pipe, 302
Pitman, 432
Plenz, 7
Pleyer, 381
Poleck, 175, 351
Pollak, 218, 222
Porter, 145, 444, 456, 457
Potane, 239
Pouchon, 439, 441
Powell, 277
Prescott, 463
Preusse, 13
Pring, 189, 190, 193, 194
Purdy, 241

R

Raken, 249
Ramsay, 12, 16, 45, 53, 209, 455, 456, 458
Rao, 194, 195
Raoult, 73
Raschig, 287
Rauch, 403
Rayleigh, 209, 437, 458
Reckleben, 221, 308, 309
Reeves, 303, 463
Regnault, 401
Reich, 284, 285, 286
Reverdine, 238
Reynolds, 194, 240
Rhodes, 148, 272
Richardson, 219
Richardt, 152, 153
Rideal, 163, 239, 401
Ridyard, 108
Ries, 290
Riesenfeld, 26
Riffe, 188
Ringe, 214
Rischbieth, 147
Ritter, 55
Riviere, 422
Robertson, 136, 342, 456, 457
Rodhe, 312
Rogatz, 382
Rogers, 412
Rolland, 73
Rosa, 335, 336
Roscoe, 301
Rosencrans, 421
Ross, 267
Rossel, 386
Rothkopf, 342
Rothmund, 194
Rüdorff, 337
Ruston, 395
Rutten, 349
Ryder, 460

S

Saillard, 290
Sainte-Claire-Deville, 341
Samter, 315, 316
Samtleben, 271
Sander, 289
Sanders, 431
Sandiford, 396
Sandmeyer, 241
Sandriset, 386

Sanford, 246, 247
Sanfourche, 227, 228
Sargent, 379
Saunders, 104
Saussure, 403
Sayers, 251
Scalione, 163
Schaefer, 46
Schaer, 269, 276
Scheele, 181
Scheffler, 294
Scheiber, 265, 266
Schelhardt, 27
Scherb, 162
Scheurer-Kestner, 157
Schilling, 50
Schleiermacher, 444
Schlösing, 73, 184
Schmalfuss, 172
Schmid, 254
Schmidt, 290
Schmolke, 344
Schmutz, 303
Schönbein, 189, 224
Schuftan, 163
Schulze, 266
Schumacher, 7, 359
Schwartz, 292
Seelig, 293
Seidell, 248, 287
Senften, 432
Shakespear, 323, 445, 449, 450
Sharp, 27
Shattuck, 27
Shaw, 425
Shenstone, 105
Shepard, 109, 258, 456, 457
Shipley, 179
Shurgar, 2
Shuttleworth, 342
Siebert, 4, 74, 136, 137, 313, 363, 437, 442, 456, 457
Siegert, 316
Sieverts, 276
Simmance-Abady, 379
Sims, 284
Sinnatt, 248
Skirrow, 271
Skossarewski, 444
Smith, 44, 104, 348
Smits, 249
Snelling, 432
Sodeau, 74
Sommerville, 279, 351
Somzie, 444
Speck, 175
Spencer, 117
Squire, 224
Starck, 297
Stavorinus, 339
Steglich, 149
Stern, 379
Steuer, 149, 172, 180
Stevenson, 218, 219
Stillman, 34
Stock, 55, 56, 110, 111, 293, 306, 456, 458
Stöckmann, 157
Stokes, 262
Stoltzenberg, 455
Stone, 280, 356, 366
Storm, 432, 436
Strache, 364, 366
Struve, 189
Stuckert, 437
Stuer, 290
Suida, 262, 264
Suydam, 74
Sveda, 142, 163
Swain, 3, 7
Swanson, 13, 15
Sweeney, 288

T

Tamele, 142
Taplay, 160

Tashiro, 419
Taylor, 44, 104, 108, 160, 161, 163, 166, 239, 263, 325, 336, 341, 431, 432
Teague, 239
Teclu, 141, 205
Teitsworth, 243
Telghman, 382
Terreil, 223
Terres, 160, 223
Than, 342
Thiele, 232
Thomas, 27, 444
Thompson, 13
Thomson, 458
Thorne, 232
Tiddy, 140
Tiemann, 13
Timiriazeff, 463
Timofejeff, 198
Titoff, 289
Titus, 243
Töpler, 8
Torwogt, 249
Tower, 396, 431
Trautzl, 193, 194
Travers, 8, 12, 16, 184, 211, 214, 215, 455, 458
Treadwell, 191, 192, 193, 215, 218, 222, 223, 224, 262, 298, 299, 300
Tropsch, 88
Trumbull, 267
Tubandt, 425
Tutweiler, 280
Tyson, 444

U

Ubbelohde, 26, 159, 164, 316
Ulex, 113
Usher, 194, 195

V

Vail, 347
Valentiner, 438
Van Brunt, 185
Vandenberghe, 237
van der Waals, 135
Venturi, 27
Vershaffelt, 40
Viehoff, 317
Vignon, 259
Vilbrandt, 101
Violette, 113
Vogel, 264, 281, 387
Volhard, 302
von Antropoff, 107
von der Pfordten, 188
von Dumreicher, 216
von Eyndhoven, 349
von Jolly, 184
von Knorre, 158, 159, 217, 386
von Kovacs-Zorkoczy, 180

W

Wachendorff, 344
Wagner, 84, 216, 436
Waidner, 24, 366
Wailes, 52
Walker, 395, 406, 408
Wallis, 272
Walter, 24
Walters, 114
Waran, 105
Wartenburg, 172
Watson, 184
Watts, 422
Weaver, 100, 147, 150, 266, 351, 358, 364, 421, 445
Webb, 431
Weibel, 421
Wein, 162, 239
Weinhold, 115
Weiskopf, 246
Weisz, 425
Wellers, 264, 267
Wempe, 74

Werner, 172, 442
Wesely, 262, 264
Weyl, 190
Weyle, 174
Weyman, 384
Weymouth, 55
Wheller, 88, 104, 134, 400, 401
White, 3, 58, 60, 140, 141, 142, 148, 150, 173
Whiton, 342, 456
Wibant, 160
Wild, 113, 190
Wilfarth, 224, 225
Williams, 13, 74
Willstätter, 266, 267
Wilmet, 278
Wilson, 41, 52, 110
Wing, 27
Winkelmann, 311
Winkler, 2, 12, 91, 121, 143, 152, 198, 220, 233, 240, 241, 254, 278, 290, 297, 302
Winmill, 248
Withrow, 288
Witzeck, 292, 351
Wohl, 135
Wolff, 114, 234, 442
Wollard, 38
Wollers, 162, 242, 244, 456
Woodhouse, 219
Worrell, 160
Worstall, 261
Wright, 281
Wug, 280
Wunsch, 162
Wurster, 190

Y

Yablick, 310
Yant, 251
Yoe, 26
Young, 356

Z

Zeally, 172
Zeitler, 174
Zenghelis, 198
Zerbe, 344
Zimmer, 438
Zimmermann, 266

INDEX OF SUBJECTS

A

Absolute and relative humidity, 396
Absorbable gases in coal gas, determination of the, 337
Absorbents, solubility of the gases in the different, 88
Absorption apparatus for use with large volumes of gas, 118
Absorption of a gas, 68
Absorption pipettes, 101
  Hempel double, 63
  Hemple simple, for solid and liquid reagents, 63
Absorption of reagent, specific, 85
Accuracy of analyses with the Hempel apparatus, 71
Acetylene, 264, 385
  determination of, 265
  determination of ammonia in, 387
  determination of carbon monoxide in, 394
  determination of ethylene in presence of, 263
  determination of hydrogen in, 386
  determination of methane in, 386
  determination of oxygen and nitrogen in, 387
  determination of phosphine in, 387
  determination of silicon hydride, in 393
  determination of sulphur in, 393
  impurities in commercial, 385
  properties of, 264
Acetylene evolved from sample of carbide, determination of volume of, 392
Ados apparatus, 319
Air, composition of atmospheric, 395
  examination of atmospheric, 395
  methods employed in determination of carbon dioxide in, 403
Ammonia, 229
  detection of, 229
  properties of, 229
Ammonia in acetylene, determination of, 387
Analyses with Hempel apparatus, accuracy of, 71
Aneroid barometer, 33
Apparatus, Hempel, accuracy of analyses with, 71
  construction and connection of, 105
  Hempel, manipulation of, 66
  mounting of, 106
Apparatus for gas analysis with water as the confining liquid, 58
Apparatus, Orsat, 73
  Bureau of Mines form, 82
  manipulation of, 79
Aqueous vapor, tension of, in inches of mercury, 473
  tension of, in millimeters of mercury, 471
Argon, 215
Argon group, 215
  argon, 215
  helium, 215
  krypton, 215

  neon, 215
  xenon, 215
Argon group, separation of nitrogen from, 215
Arrangement and fittings of the laboratory, 56
Arsine, 308
  detection of, 308
  determination of, 309
  properties of, 308
Aspirators, 6
Atomic weights, 465
Atmosphere, determination of carbon dioxide in the, 402
  determination of moisture in the, 396
Atmospheric air, composition of, examination of, 395
Autolysator, 320
Automatic flue gas analysis, 315
Automatic and recording gas calorimeters, 381
Average sample, 5
Azotometer, 436

B

Barometer, aneroid, 33
  mercurial, 34
Barometric readings, complete correction of, 43
  correction of, 34
Barometry, 33
Benzene in coal gas, absorption of, by paraffin oil, 342
  absorption with nickel solution of, 339
  absorption by alcohol of, 338
  condensation of, 341
  determination of, 338
  determination of, by absorption with charcoal, 344
  determination of, by differential pressure method, 344
Benzene, determination of, as dinitrobenzene in coal gas, 343
  separation of ethylene from, 263
  separation of, from ethylene in coal gas, 343
"Bi-meter CO_2 recorder," 319
Bone and Wheeler's apparatus, 103
Boyle, law of, 29
British thermal unit, 365
Bureau of Mines form of Orsat apparatus, 82
Buoyant effect, determination of the specific gravity of a gas by, 53
Burettes, graduation of, 88
Butylene, separation of ethylene from, 264

C

Calcium carbide, sampling of, 385
Calculation of net heating value, 378
Calculation of total heating value, 376
Calorie, 364
  large, 365
  small, 364
Calorimeters, accuracy of, 372
  automatic and recording gas, 381
  continuous flow, 365
  discontinuous, 381
Capillary depression, 38
Capillary error of the apparatus, 91
Carbon dioxide, 231
  determination of, 231
  determination of, by absorption, 318
  determination of, by electrometric methods, 325
  determination of, by optical refractivity, 324

determination of, by thermal conductivity, 323
determination of, from the specific gravity, 316
Haldane apparatus for determination of, 417
Hess method for determination of, 403
Pettersson-Palmqvist method for determination of, 408
properties of, 231
Carbon dioxide in air, methods employed in determination of, 403
Carbon dioxide in the atmosphere, determination of, 402
Carbon dioxide in coal gas, determination of, 337
"CO_2 thermoscope," 323
Carbon disulphide, 281
detection of, 281
determination of, 282
properties of, 281
Carbon monoxide, 232
colorimetric determination of, 249
detection of, by absorption, 240
detection of, by blood spectrum, 233
detection of, by iodine pentoxide, 238
determination of, by fractional combustion, 253
determination of, by iodine pentoxide, 246
properties of, 232
Carbon monoxide in acetylene, determination of, 394
Carbon monoxide in coal gas, determination of, 345
Carbon oxysulphide, 290
determination of, 292
properties of, 290
Charcoal, determination of benzene in coal gas, by absorption with, 344
Charles, law of, 30
Chlorine, 297
determination of, 297
properties of, 297
Chromous chloride, determination of oxygen with, 188
Coal gas, 334
absorption of benzene by alcohol in, 338
absorption of benzene with nickel solution in, 339
absorption of benzene by paraffin oil in, 342
condensation of benzene in, 341
constituents of, 336
determination of the absorbable gases in, 337
determination of benzene in, 338
determination of benzene by differential pressure method in, 344
determination of benzene as dinitrobenzene in, 343
determination of carbon dioxide in, 337
determination of cyanogen in, 362
determination of the illuminating power of, 335
determination of naphthalene in, 348
determination of nitrogen in, 347
determination of the specific gravity of, 336
determination of sulphur by Referees method in, 359
determination of sulphur in, by the U. S. Bureau of Standards (Drehschmidt) method, 351

  determination of tar vapors in, 362
  determination of total sulphur in, 350
  gas-volumetric analysis of, 336
  gravimetric determination of sulphur in, 355
  heavy hydrocarbons in, 344
  separation of benzene from ethylene in, 343
  turbidimetric determination of sulphur in, 358
  volumetric determination of sulphur in, 356
Coefficients of expansion, 31
Coil, induction, 141
Collection of gases dissolved in liquids, 12
Collection of gases from reactions in sealed tubes, 15
Collection of gases from springs, 11
Collection and storage of gases, 1
Colloidal palladium, 201
Colorimetric determination of carbon monoxide, 249
Combustion, analysis by, 143
  determination of gases by, 138
  fractional, of hydrogen with copper oxide, 157
  fractional, of hydrogen, 208
  fractional, with platinum or palladium asbestos, 151
  heat of, 373
Combustion of gas mixtures containing nitrogen, 124
Combustion of gases, 123
  first case, 126
  second case, 129
  third case, 129
  fourth case, 131
Combustion of gases containing carbon, hydrogen and oxygen, 124
Combustion of hydrocarbons, 123
Combustion with a platinum capillary tube, 149
Combustion pipette, 143
  determination of hydrogen with, 206
  formation of oxides of nitrogen in, 148
Complete correction of barometric readings, 43
Composition of atmospheric air, 395
Condensation of benzene in coal gas, 341
Confining liquid, apparatus for gas analysis with water as, 58
  running-down of, 93
  solubility of gases in, 87
Connections, rubber, 106
Construction and connection of apparatus, 105
Continuous flow calorimeters, 365
Copper, determination of oxygen with, 184
Copper eudiometer, determination of oxygen with, 173
Copper oxide, fractional combustion of hydrogen with, 157
Correction of barometric readings, 34
  complete, 43
Correction for gravity, 34
Correction for the measured height of the mercury column, 37
Corrections for observed heating values of illuminating gas, 377
Corrections for observed heating values of natural gas, 378
Correction for the temperature of the mercury, 36
Correction tube, gas burettes with, 95
Cuprous chloride, preparation of, 243

Cyanogen, 268
  detection of, 268
  detection and determination of, in presence of hydrogen cyanide, 272
  determination of, 270
  determination of, in coal gas, 362
  properties of, 268

D

Dennis form, Orsat apparatus, 78
Densities of gases, theoretical, 466
Density of gas, determination of, 49
Density and specific gravity of gases, determination of, 49
Depression, capillary, 38
Dichloro-ethylsulphide, 310
Differential pressure method in coal gas, determination of benzene by, 344
Diffusion, 458
Dinitrobenzene, determination of benzene as, in coal gas, 343
Direct weighing, determination of the specific gravity of a gas by, 49
Discontinuous calorimeters, 381
Distillation, fractional, of gases, 455
Drawing off the sample, 1
Drehschmidt method, determina- the specific gravity of a gas by, the, 351
Dry gas meter, 24
Dry and welt bulb thermometers, 396

E

Effect of pressure upon volume of gas, 29
Effect of temperature upon volume of gas, 29
Effusion method, determination of the specific gravity of a gas by, 50
Ethane in coal gas, determination of, 345
Ethylene, 262
  determination of, by absorption, 262
  determination of, in presence of acetylene, 263
  properties of, 262
  separation of, from benzene, 263
  separation of, from butylene, 264
Ethylene in coal gas, separation of benzene from, 343
Expansion, coefficients of, 31
Expansion of the scale, 37
Explosion, determination of hydrogen by, 205
  proportion of gases in analysis by, 140
Exact gas analysis with mercury as confining liquid, Hempel, 94
Extraction of gases from minerals, 16

F

Factors affecting the accuracy of analyses of gases, 85
  capillary error of the apparatus, 91
  changes of temperature and pressure, 86
  change in the water-vapor content, 87
  graduation of the burettes, 88
  running-down of the confining liquid, 93
  solubility of gases in the confining liquid, 87

  solubility of the gases in the different absorbents, 88
  specific absorption of the reagent, 85
Ferrous salts, determination of oxygen with, 186
Float valve, mercury, 110
Flow calorimeters, continuous, 365
Flow meter, 26
Flue gas analysis, 311
Flue gas, analysis of, 313
  automatic analysis of, 315
  sampling of, 312
Flue gas analyzers, automatic, 319
Flue gas calculations, 325
  excess air, 327
  heat loss in flue gas, 330
  weight of air for combustion, 326
  weight of flue gas, 329
Fluorine, 294
  determination of, 294
Fractional combustion, determination of carbon monoxide by, 253
Fractional combustion of hydrogen, 208
  with copper oxide, 157
  with palladium black, 155
Fractional combustion with platinum or palladium asbestos, 151
Fractional distillation of gases, 455
Fuel gas, 334

G

Gas analysis, apparatus for, with water as the confining liquid, 58
Gas burettes with correction tube, 95
Gas meter, 21
Gas pipettes, 60
Gas volumeter, Lunge, 425
Gas-volumetric analysis, 422
  of coal gas, 336
Gas washing-bottles, 118
Gases, collection and storage of, 1
  factors affecting the accuracy of analyses of, 85
  methods for determination of, 171
  specific heats of, 331
  storage of, 1
Gases dissolved in liquids, collection of, 12
Gases from minerals, extraction of, 16
Gases from reactions in sealed tubes, collection of, 15
Gases from springs, collection of, 11
Gasometers, 18
Gauge, McLeod, 45
Glass to metal joints, 108
Graduation of the burettes, 88
Gravimetric determination of sulphur in coal gas, 355
Gravity, correction for, 34
Ground-glass joints, 107

H

Haldane apparatus for determination of carbon dioxide, 417
Heat of combustion, 373
Heating value, calculation of, 384
  calculation of net, 378
  calculation of the observed, 374
  calculation of the total, 376
  net, 374
  observed, 374
  total, 373
Heating value of gas, determination of, 364, 371
Heating values of illuminating gas, corrections for observed, 377

Heating values of natural gas, corrections for observed, 378
Heavy hydrocarbons in coal gas, 344
Height of the mercury column, correction for, 37
Helium, 215
Hempel apparatus, accuracy of analyses with, 71
  for exact gas analysis with mercury as confining liquid, 94
  manipulation of, 66
  modifications of, 72
Hempel double absorption pipettes, 63
  for liquid reagents, 64
  for solid and liquid reagents, 65
Hempel simple absorption pipettes, 60
Hess method for determination of carbon dioxide, 403
Humidity, absolute and relative, 396
Hydrocarbons, absorption of heavy, 260
  in coal gas, 344
  combustion of, 123
  heavy, 259
  identification of gaseous, 134
Hydrogen in acetylene, determination of, 386
Hydrogen, detection of, 198
  determination of, by absorption, 199
  determination of, with combustion pipette, 206
  determination of, by explosion, 205
  fractional combustion of, 208
  fractional combustion of, with copper oxide, 157
  fractional combustion of, with palladium black, 155
  properties of, 197
Hydrogen chloride, 301
  determination of, 302
  properties of, 301
Hydrogen cyanide, 275
  detection of, 275
  detection and determination of cyanogen in presence of, 272
  determination of, 277
  properties of, 275
Hydrogen cyanide in air, detection of, 276
Hydrogen and oxy-hydrogen gas, preparation of pure, 142
Hydrogen sulphide, 278
  detection of, 278
  determination of, 279
  properties of, 278

I

Illuminating gas, 334
Illuminating power of coal gas, determination of the, 335
Identification of gaseous hydrocarbons, 134
Induction coil, 141
Interferometer, 439
  applications of, 444
  calibration of, 442
  operation of, 443
Iodine pentoxide, detection of carbon monoxide by means of, 238
  determination of carbon monoxide by, 246

J

Joints, glass to metal, 108
  ground-glass, 107

K

Katharometer, 449

  applications of, 453
  balanced bridge for, 452
  calibration of, 451
  unbalanced bridge for, 452
Krypton, 215

L

Laboratory, arrangement and fittings of, 56
Large calorie, 365
Law of Boyle, 29
Law of Charles, 30
Liquid reagents, Hempel double absorption pipette for, 64
  Hempel simple absorption pipette for, 60
Liquids, collection of gases dissolved in, 12
Lubrication of stopcocks, 108
Lunge gas volumeter, 425
Lunge nitrometer, 422
  manipulation of the, 423

M

Manipulation of the Hempel apparatus, 66
Manometry, 44
McLeod gauge, 45
Measurement of 100 cc. of a gas, 67
Measurement of large samples of gas, 21
Meniscus correction, 89
Mercurial barometer, 34
Mercury, correction for the temperature of, 36
  purification of, by concentrated sulphuric acid and mercurous sulphate, 114
  purification of, by distillation, 115
  purification of, by nitric acid, 113
  vapor pressure of, 38
Mercury absorption pipette with absorption bulb, 102
Mercury absorption pipette, simple, 101
  for solid and liquid reagents, 102
Mercury float valve, 110
Mercury pump, 8
Mercury seals, 107
Meter, dry gas, 24
  flow, 26
  gas, 21
Methane, 254
  detection of, 255
  determination of, 255
  properties of, 254
Methane in acetylene, determination of, 386
Methane in coal gas, determination of, 345
Methyl chloride, 303
  determination of, 304
  properties of, 303
Micro-analysis of gases, 459
  by method of constant pressure, 463
  by method of constant volume, 459
Minerals, extraction of gases from, 16
Moisture in the atmosphere, determination of, 396
Molecular volumes of gases, 134
Mounting of apparatus, 106
Mustard gas, 310

N

Naphthalene in coal gas, determination of, 348
Natural gas, 334, 362
Neon, 215

Net heating value, 374
  calculation of, 378
Nickel solution, absorption of benzene with, in coal gas, 339
Nitric oxide, 220
  detection of, 220
  determination of, 222
  properties of, 220
Nitrogen, absorption of, 209
  combustion of gas mixtures containing, 124
  formation of oxides of, 141
  properties of, 209
  separation from argon group, 215
Nitrogen in acetylene, determination of oxygen and, 387
Nitrogen in coal gas, determination of, 347
Nitrogen peroxide, 228
  properties of, 228
Nitrometer, 428
  Dennis, 428
  DuPont, 432
  DuPont, standardization of, 434
  DuPont, standardization of, with dry air, 434
  DuPont, standardization of, with potassium nitrate, 435
  Lunge, 422
Nitrous oxide, 215
  detection of, 216
  determination of, 216
  properties of, 215

O

Observed heating value, 374
  calculation of, 374
Observed heating values of illuminating gas, corrections for, 377
Observed heating values of natural gas, corrections for, 378
Orsat apparatus, 73
  Bureau of Mines form, 82
  Dennis form, 78
  manipulation of, 79
Oxides of nitrogen, formation of, 141
  formation of, in combustion pipette, 148
Oxygen, detection and determination of small quantities of, 171
  determination of, 172
  determination of, with chromous chloride, 188
  determination of, with copper, 184
  determination of, with copper eudiometer, 173
  determination of, with ferrous salts, 186
  determination of, with phosphorus, 181
  determination of, with sodium hyposulphite, 187
  properties of, 171
Oxygen, determination of, by absorption, 174
  with alkaline pyrogallol, 174
  with chromous chloride, 188
  with copper, 184
  with ferrous salts, 186
  with phosphorus, 181
  with sodium hyposulphite, 187
Oxygen in coal gas, determination of, 345
Oxygen and nitrogen in acetylene, determination of, 387
Oxy-hydrogen gas, preparation of pure hydrogen and, 142
Ozone, 189
  detection of, 189
  determination of, 191
  properties of, 189

P

Palladium asbestos, fractional combustion with, 151
Palladium-black, 199
  fractional combustion of hydrogen with, 155
Palladium, colloidal, 201
Pettersson-Palmqvist method for determination of carbon dioxide, 408
Phosgene, 302
  detection of, 302
  determination of, 303
  properties of, 302
Phosphine, 305
  determination of, 306
  properties of, 305
Phosphine in acetylene, determination of, 387
Phosphorus, determination of oxygen with, 181
Physical methods of gas analysis, 437
Pipette, combustion, 143
  combustion, determination of hydrogen with, 206
  Hempel double absorption, for liquid reagents, 64
  Hempel double absorption, for solid and liquid reagents, 65
  for liquid reagents, Hempel simple absorption, 60
  manipulation of the combustion, 145
  mercury absorption, with absorption bulb, 102
  simple mercury absorption, 101
  simple mercury absorption, for solid and liquid reagents, 102
  for solid and liquid reagents, Hempel simple absorption, 63
Pipettes, absorption, 101
  gas, 60
  Hempel double absorption, 63
  Hempel simple absorption, 60
Platinum asbestos, fractional combustion with, 151
Platinum capillary tube, combustion with, 149
Properties of gases, determination of, 171
Proportion of gases in analysis by explosion, 140
Propylene, 264
Psychrometer, manipulation of the, 398
Psychrometers, 397
Pump, mercury, 8
  Töpler, 8
Purification of mercury, 112
Pyrogallol, determination of oxygen with, 174

R

Recording and automatic gas calorimeters, 381
Reduction of a volume of gas to standard conditions, 29
Refractivity, 437
  of gases, 442
Referees method, determination of sulphur by, in coal gas, 359
Relative humidity, absolute and, 396
Rotameter, 27
Rubber connections, 106
Running-down of the confining liquid, 93

S

Sample, average, 5
  drawing off, 1
Sample tubes, 3
Samples of gas, measurement of large, 21
Sampling of calcium carbide, 385

Sampling of flue gas, 312
Scale, expansion of, 37
Sealed tubes, collection of gases from reactions in, 15
Seals, mercury, 107
Silicon hydride in acetylene, determination of, 393
Silicon tetrafluoride, 305
  properties of, 305
Small calorie, 364
Sodium hyposulphate, determination of oxygen with, 187
Solid and liquid reagents, Hempel double absorption pipette for, 65
  Hempel simple absorption pipette for, 63
Solubility of gases in the confining liquid, 87
Solubility of the gases in the different absorbents, 88
Specific absorption of the reagent, 85
Specific gravity of a gas, determination of, 419
  by buoyant effect, 53
  by direct weighing, 49
  by effusion method, 50
Specific gravity of coal gas, determination of, 336
Specific heats of gases, 331
Spectrum of blood, detection of carbon monoxide by, 233
Spiral washing-bottle, 119
Springs, gases from, collection of, 11
Standard conditions, reduction of a volume of gas to, 29
Stibine, 309
  properties of, 309
Stopcocks, 108
  lubrication of, 108
Storage of gases, 1
Sulphur, determination of, in coal gas, by Referees method, 359
Sulphur in acetylene, determination of, 393
Sulphur in coal gas, determination of, U. S. Bureau of Standards (Drehschmidt) method, 351
  gravimetric determination of, 355
  turbidimetric determination of, 358
  volumetric determination of, 356
Sulphur dioxide, 283
  determination of, 283
  properties of, 283

T

Tar vapors in coal gas, determination of, 362
Tension of aqueous vapor in inches of mercury, 473
Tension of aqueous vapor in millimeters of mercury, 471
Temperature and pressure, changes of, 86
Theoretical densities of gases, 466
Thermal conductivities of gases and vapors, 447
Thermal conductivity, 444
Thermal unit, British, 365
Thermometers, wet and dry bulb, 396
Töpler pump, 8
Total heating value, 373
  calculation of, 376
Total sulphur in coal gas, determination of, 350
Tubes, sample, 3
Turbidimetric determination of sulphur in coal gas, 358

U

"Uehling CO_2 recorder," 321

V

Valve, mercury float, 110
Vapor pressure of mercury, 38
Volume of gas, effect of pressure upon, 29
  effect of temperature upon, 29
Volumeter, Lunge gas, 425
Volumetric determination of sulphur in coal gas, 356

W

Washing-bottle, gas, 118
  spiral, 119
Water-vapor content, change in, 87
Wet and dry bulb thermometers, 396

X

Xenon, 215

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